Aalto University
School of Chemical
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School of Chemical Technology
Degree Programme of Chemical Technology

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MEASURING THE RATE OF DISSOLUTION OF POLYACRYLAMIDE

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, July 27, 2015.

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Abstract of master's thesis

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Abstract

The aim of this thesis was to find a reliable method for assessing the dissolution rate of ionic polyacrylamides by studying and comparing different measuring methods.

Ionic polyacrylamides (PAM) are used as auxiliary substances in various processes such as in wastewater treatment and paper industry. These ionic copolymers of acrylamide have the ability for example to agglomerate particles by flocculation due to the large molecular mass and the charges of the ionic groups. Good solubility of PAM is extremely important for its applications, as the undissolved particles can weaken the performance of the polymer. Sometimes polymerization produces partly insoluble polymers or slowly dissolving polymer fractions. Nevertheless, the solubility might exceed to the necessary level, though the dissolution may require more time than usual. Therefore, it is necessary to assess the rate of dissolution.

There is no established practice on how to measure the rate of the dissolution of PAM. In this report three different methods were assessed and compared with each other. The used methods were optical measuring system, torque measurements with a stirrer and viscosity measurements with a rotational viscometer. The optical measuring system measures the intensity of a laser light passing through the solution mixture. The torque stirrer measures the torque of the impeller stirring the solution mixture and the rotational viscometer measures the apparent viscosity of the solution during the dissolution.

With both the optical measuring system and rotational viscometer the dissolution rates for different samples could be distinguished from each other. In torque stirrer measurements the differences between fast and slow dissolving samples were not observed as well and the obtained dissolution times for the samples were much shorter than the defined dissolution times.

The rotational viscometer was the most accurate for determining the dissolution rate of PAM. With rotational viscometer the dissolution rates of different samples could be clearly distinguished and the endpoint of the dissolution was relatively easy to assess as the viscosity values stabilized.

Keywords Polyacrylamide, solubility, dissolution rate, optical measuring system, Keyence, torque, rotational viscometer, Brookfield

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Tiivistelmä

Tämän työn tarkoituksena oli löytää luotettava menetelmä ionisten polyakryyliamidien liukenemisnopeuden mittaamiseksi.

Ionisia polyakryyliamideja (PAM) käytetään useissa erilaisissa prosesseissa kuten vedenpuhdistuksessa ja paperiteollisuudessa. Näitä ionisia kopolymeerejä voidaan niiden korkean molekyylipainon ja ionisten ryhmien varausten ansiosta hyödyntää esimerkiksi flokkauksessa, jossa kiintoaineita erotetaan nesteestä. PAM:n hyvä liukoisuus on erityisen tärkeää sitä käyttäville sovelluksille, koska liukenemattomat partikkelit voivat heikentää polymeerin tehokkuutta. Joskus polymerisaatiossa syntyy liukenemattomia tai hitaasti liukenevia polymeerifraktioita. Niistä huolimatta tarvittava liukoisuustaso saatetaan saavuttaa, mutta liukeneminen voi kestää kauemmin kuin tavallisesti. Tämän takia liukenemisnopeuden mittaaminen on tarpeen.

PAM:n liukenemisnopeuden mittaamiseen ei ole vakiintunutta menetelmää. Tässä työssä kolme erilaista mittausmenetelmää arvioitiin ja niitä vertailtiin toisiinsa. Käytetyt menetelmät olivat optinen mittaus, vääntömomentin mittaus sekoittimella sekä viskositeetin mittaus viskometrillä. Optinen mittaus mittaa liuoksen läpi kulkevan laservalon intensiteettiä. Vääntö-momenttisekoittimella mitattiin sekoitinvarren vääntömomenttia ja viskometrillä mitattiin liuoksen näennäisviskositeettia liukenemisen aikana.

Eri näytteiden liukenemisnopeudet pystyttiin erottamaan toisistaan sekä optisella mittauksella että viskometrillä. Vääntömomenttimittauksissa eroja nopea- ja hidasliukoisten näytteiden välillä ei pystytty näkemään yhtä hyvin ja lisäksi saadut liukenemisajat olivat paljon tiedettyjä aikoja lyhyemmät.

Viskometri oli tarkin menetelmä PAM:n liukenemisnopeuden määrittämiseen. Viskometrillä eri näytteiden liukenemisnopeudet olivat helposti erotettavissa ja lisäksi liukenemisen päätepiste oli suhteellisen helppo arvioida viskositeetin tasaantumisesta.

Avainsanat Polyakryyliamidi, liukoisuus, liukenemisnopeus, optinen mittaus, Keyence, vääntömomentti, viskometri, Brookfield

Preface

The research was carried out at Kemira's Research and Development Center in Espoo during the time period of January to June 2015.

I would like to thank my thesis supervisor Professor Ari Koskinen for his advice and support. I also want to thank my instructor Jonni Ahlgren for all the discussions and guidance during the thesis. The various discussions were interesting and helped me to deepen my understanding of the subject.

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Thank you all my friends for your support during this work. Special thanks to my dearest friend Lotta Wuolamo who read my thesis and gave me valuable feedback several times.

Finally, I thank my family for the support that they have given me during my studies. Great thanks to my husband Juho for his encouraging attitude and for being awesome.

Espoo, July 17, 2015

Emilia Jyrkiäinen

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List of abbreviations

DI H_2O	deionized water
DLS	dynamic light scattering
FBRM	focused beam reflectance measurement
LD	laser diffraction
PAM	ionic polyacrylamide
rt	room temperature
UAS	ultrasonic attenuation spectroscopy
wt%	weight percent

1 Introduction

Ionic polyacrylamides (PAM) are used as auxiliary substances in various applications. Ionic PAM has the ability for example to agglomerate particles and neutralize charged surfaces through the ionic groups of the polymer.

Good solubility of PAM is extremely important for its applications, as the undissolved particles can weaken the performance of the polymer. Sometimes polymerization produces partly insoluble polymers or slowly dissolving polymer fractions. Nevertheless, the solubility might exceed to the necessary level, though the dissolution may require more time than usual. Therefore, it is necessary to assess the rate of dissolution.

The aim of this thesis was to find a reliable method for assessing the dissolution rate of PAM. As there was no established practice on how to measure the dissolution rate, different options were discussed in Chapter 3. From these discussed methods three were chosen for further investigation. The chosen measuring methods were optical measuring system, torque measurements with a stirrer and viscosity measurements with a rotational viscometer. These methods were assessed and compared with each other.

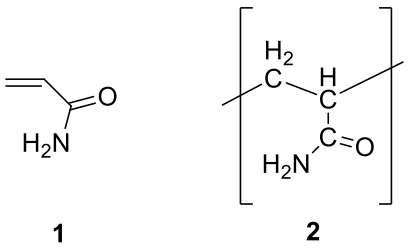
The optical measuring system measures the intensity of a laser light passing through the solution mixture. The torque stirrer measures the torque of the impeller stirring the solution mixture and the rotational viscometer determines the apparent viscosity of the solution during the dissolution.

2 Polyacrylamide, solubility & rate of dissolution

In this chapter the basics of polyacrylamides are presented and the dissolution of polyacrylamides is discussed. In the end of the chapter key factors affecting the rate of dissolution of PAM are introduced.

2.1 Polyacrylamide (PAM)

Polyacrylamide is a polymer synthesized from acrylamide. Acrylamide can be polymerized by free radical polymerization.[1,2,3] Acrylamide monomer **1** and the repeating unit of non-ionic PAM **2** are presented in **Figure 2.1**. Acrylamide monomer is carcinogenic and toxic, whereas polyacrylamide is a substance with no hazardous characteristics.[2,4,5]



1 **2**

Figure 2.1 Acrylamide monomer and the repeating unit of non-ionic PAM.

Even though the name polyacrylamide is used, PAM usually stands for ionic copolymers of acrylamide. Copolymer refers to a polymer, which has two or more different kinds of monomers. Also in this thesis the abbreviation PAM refers to the ionic copolymers of polyacrylamide if not stated otherwise.

Both anionic and cationic PAM consist of two different kinds of monomers. Anionic PAM is made from acrylamide and an anionic monomer whereas cationic PAM is made from acrylamide and a cationic monomer. The repeating units of cationic and anionic PAM are presented in **Figure 2.2**. The anionic PAM is presented with sodium acrylate as the anionic monomer. Furthermore, acryloyloxyethyltrimethylammonium chloride (ADAM-

Cl) is presented as the cationic monomer as it was used in this research. Nevertheless, it should be noted that also other monomers can be used such as methacrylamidopropyltrimethylammonium chloride (MAPTAC)[2].

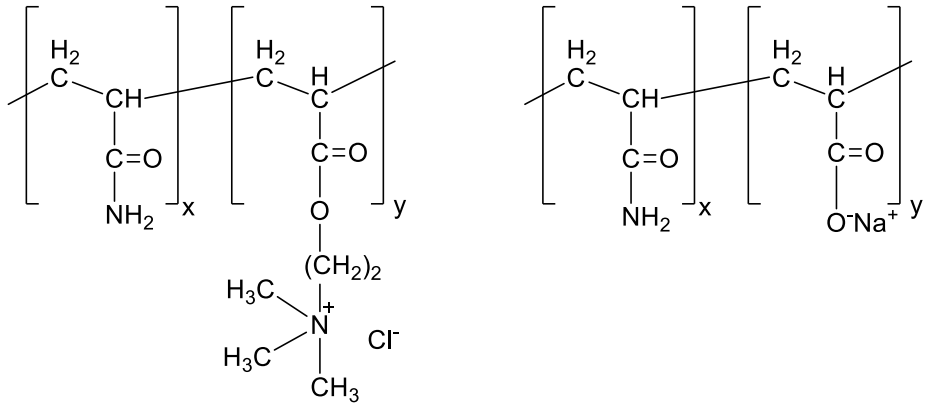


Figure 2.2 Repeating units of cationic PAM **3** and anionic PAM **4**.

Charged water soluble polymers are called polyelectrolytes. Thus, PAM is a polyelectrolyte as it is both charged and water soluble polymer. Solubility and the dissolution of PAM are discussed further in Chapter 2.3.

Polyacrylamides are produced by many different suppliers worldwide. PAMs are supplied in different forms such as emulsions, solutions and dry powders[1,6]. Furthermore, PAM can be bought as dry beads with the diameter range varying from 100 to 2000 µm.[2]

Ionic polyacrylamides are generally used in applications that exploit the chemistry of the charged groups. For example high molecular weight cationic PAM can attach to a large number of particles through polymer bridging. In polymer bridging the cationic polymer attracts negatively charged particles and forms bridges between these particles as shown in **Figure 2.3**. Through the ionic groups, PAM has the ability to flocculate particles and to neutralize charged surfaces.

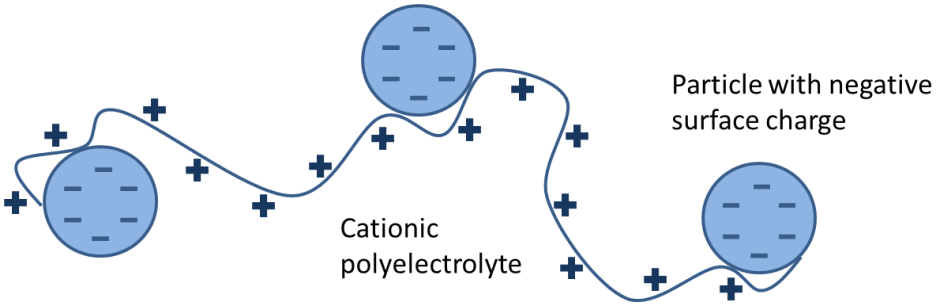


Figure 2.3 Polymer bridging.

In addition to the charge of the polymer, also the molecular weight affects the bonding ability.[1,2] The higher the molecular weight the better an individual chain can attach itself to the surrounding particles.[1] Polyacrylamides have typically high molar masses of several millions g/mol. Due to these properties PAM is useful in various industrial applications and some of them are briefly introduced in the next chapter.

2.2 Applications for PAM

Polyacrylamide is used in many industrial applications including water treatment, paper manufacturing, oil recovery and mining.

In water treatment applications PAM is mainly used as a flocculant. In flocculation the charged polymer creates larger agglomerates by connecting individual particles together as shown in **Figure 2.4**. Polyacrylamide flocculants are used for example for faster sedimentation and separating impurities by creating easily separable flocs. PAM flocculants are also used for reducing sludge volume by dewatering. In these applications mainly cationic PAM is used, as the sludge is negatively charged.[2]

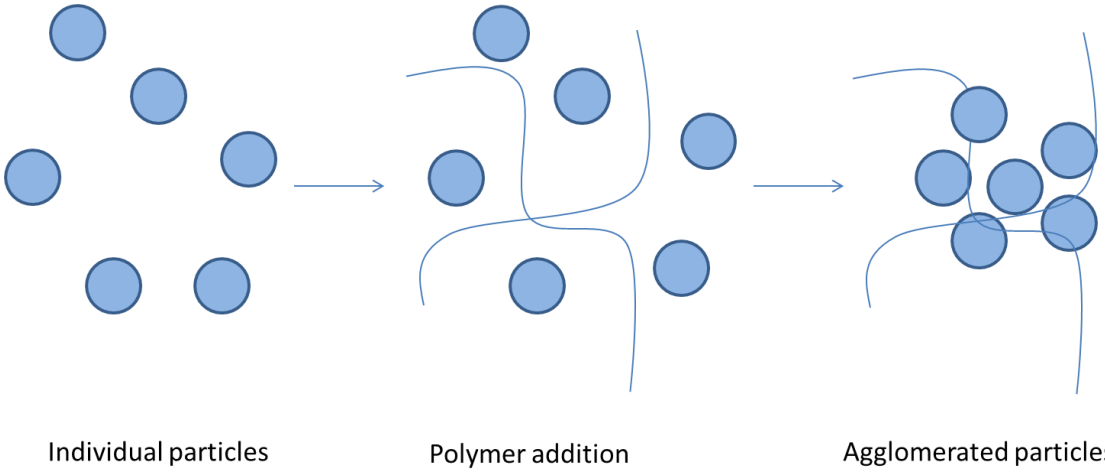


Figure 2.4 The principle of flocculation.

In paper industry ionic polyacrylamides are mainly used as retention aids. Retention aids improve drainage and retention of fibers, fillers and other fine particles in the sheet. PAM can also be used to strengthen already finished paper.[2,6]

In oil field applications, such as enhanced oil recovery, mostly anionic PAM is used. In oil recovery anionic PAM is used for polymer flooding. In the flooding process it is extremely important to avoid adsorption onto the negatively charged surface of the reservoir rock. As negative charges repel each other, anionic PAM is preferred in these applications.[2]

2.3 Solubility and rate of dissolution

Solubility is a property that describes the ability of a substance (solute) to dissolve into another (solvent) at a given temperature. Solubility is generally expressed as the mass of the solute dissolved per unit volume of solvent. The solute can dissolve either completely, partially or not at all and the incomplete dissolution of the solute could be due to insoluble solute particles. However, polymer dissolution is not as straightforward.

When high molecular weight polyacrylamide dissolves in water, the polymer first transforms into a transparent gel-like particles, which can be seen in **Figure 2.5**. These transparent polymer particles then swell and slowly dissolve into the solvent. Because

of this transitional phase, the dissolution of PAM is relatively slow. The prepared PAM solutions look like gels and even the physical properties resemble each other.[1]

Figure 2.5 Cationic PAM as transparent, gel-like particles in deionized water (DI H_2O).

Although PAM can theoretically dissolve in water, sometimes the polymerization produces partly insoluble polymers. For example the drying of polymer gels may result with degradation and insoluble or slowly dissolving polymer fractions.[1] If cross-linking of the polymer occurs, the cross-linked polymer will only swell in water without dissolving.[6]

The difference between insoluble and slowly dissolving polymer should be carefully considered. As there are several different methods how to assess the level of solubility, the result is always linked to the used method. Therefore, when insoluble polymers are discussed, it actually refers to the undissolved polymer without telling if the undissolved polymer is truly insoluble. It might be that some or all of the undissolved polymer would still dissolve over time.

Therefore, knowing the level of solubility at a certain time is not always effective, as it does not show whether the sample would have further dissolved over time. For this purpose, it is necessary to assess the rate of dissolution. The rate of dissolution describes the speed at which the solute dissolves into the solvent. However, it should be noted that it is extremely difficult to define the time at which the polymer is dissolved

completely. The size of the transparent particles decreases as the dissolution continues until even the smallest, microscopic particles are dissolved. Therefore, in this thesis the aim is not to determine when the last particle is dissolved, but to measure the dissolution rate during the dissolution in general.

2.4 Factors affecting rate of dissolution

The rate of dissolution is affected by many factors, including temperature as well as the properties of the solute and solvent. When the solute is in a solid or liquid form, changes in pressure will not notably affect the solubility. In terms of the properties of PAM, it is already known that PAM is generally soluble in water[1,2,6,7].

The following key factors affect the rate of dissolution of PAM:

- solute properties (molecular weight, charge density, particle size and surface area)
- stirring (stirring speed and stirrer)
- changes in the concentration of the solution
- dissolved salts in the solvent
- temperature
- pH

Solute properties such as molecular weight and charge density of the polymer affect the dissolution rate. Dissolution rate decreases with increasing the molecular weight of the polymer[8] and the dissolution rate increases with increasing the charge level of the polymer[9].

The particle size and surface area of the solute is one of the most important factors affecting the dissolution rate. With decreasing particle size, the surface area increases, leading to more rapid dissolution of the solute[10,11,12]. However, it has been observed that powders hydrate relatively fast which leads to formation of gelatinous clumps. Therefore, the dissolution is not necessarily easier with smaller particle size.[6]

Homogeneous mixing of the solute into the solvent requires stirring. Although increasing the stirring speed increases the dissolution rate, a high stirring speed can also degrade

the polymer and decrease the viscosity of the polymer[2]. Therefore, the optimal stirring speed needs to be determined experimentally. The effectiveness of the stirring is also related to the shape of the impeller.[13]

As the solute dissolves into the solution, the concentration of the solution changes and the rate of dissolution will decrease.[10] The rate of dissolution will also be lower if the solvent contains dissolved salts.[2]

Higher temperature increases the rate of dissolution.[10,13] The extent of the increase depends on the solute properties.

The dissolution rate of ionic compounds is especially affected by changes in pH. [10] For example, quaternary aminoester copolymers, such as cationic PAM, are sensitive to changes in pH. If a solution has a higher pH than 6, hydrolysis of the ester group occurs.[2] Therefore, it should be ensured that the pH of the solution remains acidic throughout the dissolution.

In this thesis, aging of the solution is not considered as a factor affecting the rate of dissolution, since the aging of the solution only affects the polymer properties after a period of days or weeks.[14] Therefore, aging of the solution will have no effect on the dissolution process.

3 Different methods for assessing rate of dissolution

There are different ways to assess the rate of dissolution. In this chapter several different methods are presented and the reasons behind excluding some methods are explained.

3.1 The need and criteria for the new method

Measurements of undissolved solute have been carried out at Kemira to assess the level of solubility of PAM. First the polymer sample is added to the solvent and the solution mixture is stirred for a certain time. Then the solution is poured through a sieve, and the number of undissolved particles is counted from the sieve. However, this only tells us the current solubility level but not the dissolution rate of the polymer.

In theory these measurements of undissolved solute could also be used for assessing the dissolution rate by taking samples during the dissolution process. At first, the number of undissolved particles in the sieve would be uncountable. As more time passes, more of the solute dissolves and the number of undissolved particles in the sieve will decrease. However, this method would be extremely laborious as individual samples are needed and determining the insoluble particles from the sieve is both challenging and time-consuming. Thus, another method is needed.

When assessing suitable measuring methods, some characteristics were especially desired. First of all the method should be continuous during the dissolution process. Taking individual samples is both laborious and increases the sources of error. Also simple instrumentation was preferred over complex as using complex methods is usually both more expensive and needs more data to be used accurately.

3.2 Different measurement methods

When PAM dissolves in water, a few observations can be made. First, the viscosity of the solution increases until all soluble PAM is dissolved. Second, the solution is turbid after the polymer addition, but then the solution slowly clarifies as the solute dissolves. Methods related to these two, the viscosity and turbidity of the solution are first discussed.

Furthermore, during the dissolution the concentration of PAM increases in the liquid phase. Some methods related to the increasing concentration of PAM in the liquid phase are presented as well.

3.2.1 Viscosity-related measurements

Viscometric measurements are concentrating in following the changes in the viscosity of the solution during the dissolution process. As PAM dissolves, the viscosity increases and in theory the dissolution can be considered complete when the viscosity of the solution reaches its maximum. Viscosity is affected by the molecular weight of the sample, concentration and temperature of the solution, solvent properties as well as shear rate[3,15].

Viscosity is generally expressed as the proportion of shear stress to shear rate:

$$\eta = \frac{F'}{S}$$

where η is the viscosity
F' is the shear stress
S is the shear rate

The shear rate describes the shearing of the solution, which always occurs when the solution is in motion for example because of stirring. The shear stress then describes the needed force per unit area to produce the shearing.

For Newtonian fluids the relationship of shear stress and shear rate is linear. However, PAM solutions are non-Newtonian fluids as the relationship is not constant. For non-Newtonian fluids the measured value is called apparent viscosity (η_a). Furthermore, it is known that polyacrylamide homopolymer solutions are shear-thinning, which means that the viscosity decreases when shear rate increases[3].

In general three kinds of viscometers are used for viscosity measurements: capillary, rotational and moving body viscometers. However, as only continuous viscometers can be considered for this research, only rotational viscometers are presented.

Rotational viscometers consist of two parts, where one part is put into the solution and then the movement of that part against the other is measured. To be more exact, the torque required to produce a given angular velocity in the solution mixture is measured. The measured value is dependent on the viscosity of the solution.[15] Rotational viscometers are quite simple, suitable for continuous measurements and therefore, seem suitable for this research.

However, rotational viscometers have at least two disadvantages. First of all, the viscometer sensor needs to be put into the solution, which affects the homogeneous stirring and might cause accumulation of the polymer. Second, the method does not describe if some of the solute was insoluble and therefore, the insoluble particles have to be distinguished ocularly.

Similarly to rotational viscometers, **torque stirrers** can be used for following indirectly the changes in viscosity. Torque stirrers are stirrers which measure the torque of the impeller in the solution. As the viscosity of the solution increases, the needed torque for maintaining a certain stirring speed increases as well. As stirring is needed during the dissolution, a torque stirrer is a viable option for studying the dissolution rate of PAM. Downside is that the impellers have shanks which might cause accumulation of the polymer.

3.2.2 Turbidity-related measurements

Light scattering methods have been used for studying polymer solutions for several decades.[16] In light scattering measurements a laser beam is directed through a solution into a detector. As the solute is added to the solvent, part of the light is absorbed by the solid particles and part is scattered from them. Therefore, the light transmitted to the detector has a lower intensity than before. Light scattering can be measured in different ways and the following methods are described below: Optical measuring system, dynamic light scattering (DLS) and laser diffraction (LD). Also smaller turbidity meter and focused beam reflectance measurement (FBRM) are presented.

Optical measuring system measures intensity of the laser transmitted through the solution. As the solute dissolves, more light passes through the solution without

scattering or absorbing and the intensity of the transmitted light increases. The intensity will increase until all of the solute is dissolved.[16,17] However, it should be noted that small particles with a diameter less than 2 µm might not have a measurable effect on the observed intensity.[18]

Dynamic light scattering (DLS) measures the intensity of scattered light in a certain angle (usually 90^{o}) and **laser diffraction (LD)** scattering measures the intensity of scattered light in different angles (32 or more). As the solute dissolves in the dissolution process, light scattering decreases until everything has been dissolved. With these methods it is also possible to determine particle sizes, as the scattering intensity corresponds to the size of the particle.[19] DLS and LD can also observe particles with less than 2 µm diameter.[18]

For light scattering measurements separate samples are not needed as the measurement is continuous during the dissolution process. Also there is no need for sensors in the solution and therefore, the stirring will not get affected. Moreover, with this method it is possible, at least in theory, to observe insoluble solute in the solution mixture even at the end of the dissolution, as the part of the light will scatter until everything is dissolved.

Even though optical measuring system cannot observe as small particles as DLS and LD can, the accuracy achieved with optical measuring is sufficient. Optical measuring set up is quite similar to DLS. However, as both DLS and LD measure the scattered light instead of the changes in the intensity of the transmitted laser light, the data analysis is more complex for these methods.

Also **smaller turbidity meters** could be used to assess the dissolution rate. Turbidity meters are based on measuring the loss in the intensity of the transmitted light just as optical measuring system. However, the turbidity meter has to be set into the solution mixture. This might affect the homogeneous stirring, which can cause agglomeration and in the worst case the agglomerated particles could block the sensor.

Focused beam reflectance measurement (FBRM) is also based on backward light scattering and it is generally used to determine particle size distribution. A laser beam is focused through a sapphire window into the solution. The laser beam rotates in a circular motion and whenever it comes in contact with a particle, light scatters. Part of the light is reflected back to a detector.[20,21]

FBRM can determine particle sizes between 1 to 1000 µm.[22] However, even though FBRM is as accurate as turbidimeter, it is also ten times more expensive method.[23] As there is no need to determine particle size distribution but only the proportion of undissolved PAM to dissolved PAM, FBRM will not be considered as a potential option for this research.

3.2.3 Concentration-related measurements

As ionic polyacrylamides dissolve, the amount of ions in the solution increases. This increase in the ion concentration could be measured with **conductivity measurements** as conductivity describes the concentration of ions in a solution.

Conductivity meter consists of two electrodes with a known distance. The conductivity meter is placed in the solution and as a potential is applied between them, the electric current can be measured. The electric current corresponds to the ion concentration of the solution.

As the conductivity changes during the dissolution of PAM are not known, the accuracy of the method is hard to assess without preliminary tests. However, as there are many simple and small conductivity sensors available, the suitability of the method can be assessed quite easily with preliminary tests.

Ultrasonic attenuation spectroscopy (UAS) measures the velocity and attenuation of sound waves as they move through the solution. The sound waves are attenuated according to the size and concentration of particles. As the solute dissolves, the attenuation decreases and velocity of the sound waves increase.

However, as promising as this method sounds, it has one remarkable shortcoming compared to other methods. The calculations are based on mathematical modelling[24]

and therefore, the accuracy of the measurements depends strongly on the used model. Also a lot of data about the properties of the solute and solvent are needed.[25] Furthermore, the measuring device would be placed in the solution possibly causing accumulation of the polymer and disturbance to the stirring. For these reasons UAS is not considered as a viable option for this research.

3.2.4 Combining different methods

If one method does not give enough information, combining different methods could be an option. For example viscometric measurements have been combined with water insoluble measurements in defining dissolution time of polyacrylamide[13].

It is also possible that one method is more accurate in assessing the dissolution rate in the beginning of the dissolution and another is more accurate for assessing the end of the dissolution process. Therefore, it might be that the dissolution rate should be assessed in parts: the first part when the dissolution rate is greatest and the second part, when the polymer is still dissolving, but the rate has considerably decreased compared to the first part.

3.2.5 Summary of the potential candidates

As discussed in Chapter 3.2, there are many potential methods for assessing the dissolution rate. The methods mentioned in the Chapter 3.2 are collected into **Table 3.2**. The table shows if the method was considered as a potential candidate for this research or not.

Table 3.2 Different methods and their potential for this research.

Method	Measures	Potential candidate
Rotational viscometer	Viscosity	Yes
Torque stirrer	Torque of an impeller	Yes
Optical measuring system	Intensity of transmitted light	Yes
Dynamic light scattering	Intensity of scattered light	No
Laser diffraction	Intensity of scattered light	No
Turbimeter sensor	Intensity of transmitted light	Yes
Focused beam reflectance measurement	Intensity of scattered light	No
Conductivity meter	Electronic current	Yes
Ultrasonic attenuation spectroscopy	Velocity of sound waves	No

4 Research methods and used apparatus

In Chapter 3 following methods were named as potential candidates to determine the dissolution rate of PAM:

- Rotational viscometer
- Torque stirrer
- Optical measuring system
- Turbidity meter
- Conductivity meter

From these potential methods the first three were chosen for further experiments. Turbidity meter was excluded from the chosen method as it is based on the same principle as optical measuring system, but the turbidity meter is more susceptible to accumulation of the polymer. Conductivity meter was excluded as preliminary tests showed that conductivity values fluctuated greatly during the dissolution of PAM and therefore, it was not considered accurate enough for assessing the dissolution rate.

The temperature and conductivity of the solvent were measured before every dissolution test with a conductivity meter Knick Portamess 911 Cond.

4.1 Optical measuring system

As mentioned in Chapter 3.2.2, optical measuring system measures the intensity of the laser light transmitted through the solution. The measuring system consists of a light source, light detector, windowed beaker and a magnetic stirrer. The laser apparatus along with the used data logger can be seen in **Figure 4.1.1**. The basic measuring principle is explained below along with the information about the used apparatus.

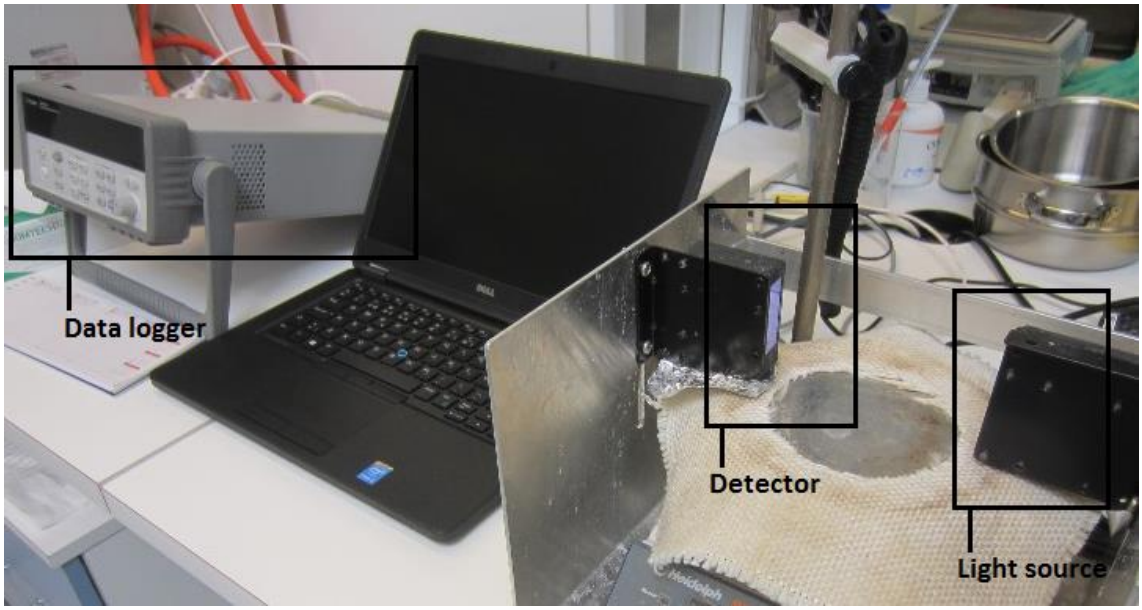


Figure 4.1.1 Laser apparatus and data logger used in the optical measuring system measurements.

As the laser beam passes through the solution, some of the light is absorbed and some is scattered due to the particles in the solution. As a result, the intensity of the transmitted laser light is reduced. When the solute dissolves, the size of the particles decreases and more light passes through the solution. As more light passes to the detector, the intensity of the transmitted light increases.

Laser apparatus Keyence sensor series IB-30 was used in the measurements. The minimum detection target diameter is 0.2 mm, which means that smaller particles do not have a measurable effect on the observed intensity. In the middle of the laser transmitter and the detector was a magnetic stirrer Heidolph MR 3001t, which was used for the stirring of the solution mixture. The Teflon coated magnet used in the measurements was 5 cm long and had a diameter of 2 cm and it can be seen in **Figure 4.1.2**. The measured data was collected with Agilent 3497A and Agilent Benchlink Data Logger 3 software.

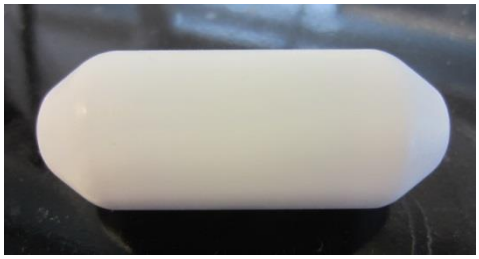


Figure 4.1.2 Magnet used in the optical measuring system measurements.

4.2 Torque stirrer

Torque stirrer measures the torque of the impeller that is stirring the solution mixture. As the viscosity of the solution increases during the dissolution, the torque needed to maintain the same stirring speed increases as well.

Torque stirrer Heidolph RZR2102 was used in the measurements. The stirrer blade used in the measurements can be seen in **Figure 4.2**. The length of the stirrer blade was approximately 7 cm and the top diameter was approximately 6 cm. The blade type was chosen due to its ability to stir effectively and because it has a large surface area. Larger surface area makes the blade more sensitive to the torque changes. The measured data was collected with a DaqPRO Datalogger 5300 and DaqLab software.

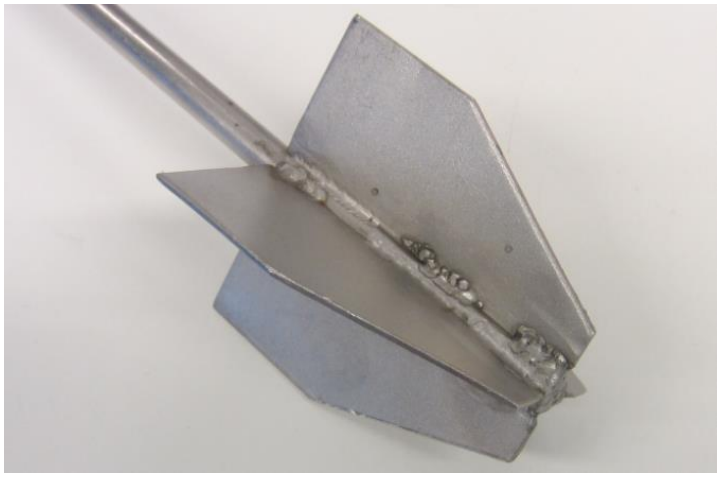


Figure 4.2 Stirrer blade used in the torque measurements.

4.2 Rotational viscometer

Rotational viscometers have separate spindles that have to be attached to the device. The spindle is attached to the viscometer by screwing the spindle to the shaft. The spindle is placed into the solution and the viscometer measures the torque required to produce a certain angular velocity. As the solute dissolves, the viscosity of the solution increases and the torque increases as well.

Brookfield DVII+ Pro Viscometer and a magnetic stirrer (IKA big squid) were used in the measurements. The spindles were chosen so that the limit of the measurement range would correspond to the maximum viscosity of the sample. The used spindles were RV2 and RV3 and the rotating speeds of the spindles were 50 and 100 rpm. The measured data was collected with a DaqPRO Datalogger 5300 and DaqLab software.

5 Performing the research and results

The samples and the tested parameters are described in Section 5.1. Then the procedures and results for each measurement method are presented.

First the procedure and results of the optical measuring system measurements are presented in Section 5.2. Second, the torque stirrer measurements are presented in Section 5.3 and the viscometer measurements can be found in Section 5.3. Conclusions from the results as well as evaluation and comparison of the methods can be found in Chapter 6.

5.1 General information about the measurements

Four different cationic polyacrylamide samples were used in the measurements and the samples were in a form of solid, white powder. The first sample S1 was chosen due to its different molecular weight level but same charge level as the sample S2. The three samples S2, S3 and S4 were chosen due to their different charge levels. These sample properties can be seen in **Table 5.1** with their defined dissolution times. The defined dissolution times have been determined with a quality control method in Kemira. Time of measurement was always 30 minutes more than the defined dissolution time to ensure that the dissolution was complete.

Table 5.1 Sample properties and defined dissolution times.

Sample	Charge level	Molecular weight level	Defined dissolution time (min)
S1	High	High	30
S2	High	Very high	30
S3	Low	Very high	60
S4	Very low	Very high	120

As the defined dissolution times for the samples S1 and S2 are the shortest, their dissolution rates should be faster than the ones for the samples S3 and S4. As the sample

S4 has the longest defined dissolution time, the dissolution rate of the sample S4 should be much slower compared to the other three samples.

First measurements were done with deionized water (DI H_2O) in room temperature. The concentration of the prepared solution was 0.5 wt% if not mentioned otherwise.

Some key factors affecting the dissolution rate mentioned in Chapter 2.4 were also tested. These measurements were done in order to determine how sensitive the different measuring methods were to parameter changes.

The effect of using different solvents, tap water and 0.05M NaCl in DI H_2O, were tested as well as different temperatures for the solvent. The solvent was held in a fridge overnight at 6 °C for the cold solvent measurements. For the warm solvent measurements, the solvent was held in a warm water bath with approximate temperature of 40 °C and during the measurement the beaker was wrapped with aluminum foil.

The effect of different stirring speeds was tested by making the dissolution tests with both 100 rpm higher and 100 rpm lower stirring speeds compared to the normal stirring speeds described in the procedures of the methods. Furthermore, the effect of the particle size was tested. In the particle size tests, a polymer sample was separated into two different fractions by sieving. Then the dissolution tests were done with the separated fractions.

The obtained dissolution times from all measurements can be found in Appendices. In Appendix 1, the obtained dissolution times and their percentage values of the defined dissolution times are presented. In Appendix 2, the obtained dissolution times are compared to the obtained dissolution time from the measurement with room temperature DI H_2O as a solvent.

5.2 Measurements with optical measuring system

5.2.1 Procedure

First the conductivity and temperature of the solvent were measured with a conductivity meter. Then 447.75 ± 0.01 g of solvent was measured into a windowed beaker and a magnet (described in Section 4.1) was added for stirring. The beaker was placed between the laser transmitter and the receiver and the laser was set to zero. Stirring was set to 550 rpm so that a vortex that reached the bottom of the beaker was formed. 2.250 g ± 0.001 g of cationic PAM granules were sprinkled to the edge of the generated vortex in approximately 6 seconds. After the addition the data collection was started and the solution mixture was stirred for 1 min. After 1 min the stirring was decreased to 350 rpm.

The time of measurement depended on the sample as mentioned in the beginning of the Chapter 5. If the signal did not stabilize in the intended measurement time, the measurement was continued. When the signal remained approximately at the same level, the polymer sample was assumed to be dissolved. Before ending the measurement the solution was checked for any undissolved particles. If undissolved particles were observed, the measurement was continued. When the polymer sample was dissolved completely, the data collection was stopped and the data was saved.

As the laser is set to zero in the beginning, the values obtained from the measurements describe the turbidity level compared to the zero level with a maximum of 100. This means that if the turbidity level is 100, no light passes through the solution to the receiver. Furthermore, if the values obtained would be negative, more light would pass through the solution than in the beginning. The value range for the measurement is from 100 to -100.

5.2.2 Results

Both averages and standard deviations of the obtained values were calculated from the measurements. The averages and standard deviations were calculated for each measurement point with the 9 following values. All of the calculations were done with Microsoft Excel.

Furthermore, as the standard deviation values fluctuated a great deal, moving average trendlines of 50 values were drawn for the standard deviation results. In Microsoft Excel, the trendline of 50 values calculates the averages using the current and the 49 following values. It can be argued that the resulting values predict the forthcoming stage instead of describing the current stage. Nevertheless, as the values were collected every second, the difference for the obtained results is insignificant. However, if the values would be collected for example every 10 seconds, the difference would be ten times greater.

In the beginning of the dissolution both average and standard deviation values are high. As the solute dissolves, the turbidity of the solution decreases and the solution becomes more homogeneous. Therefore, both the average and standard deviation values decrease until all of the solute is dissolved.

Even though the averages describe the turbidity level of the solution, the standard deviation was more useful in determining the dissolution rate. A straight line was drawn to the level where moving average of standard deviation values stabilized. The line drawn illustrated the dissolved state. The polymer was considered dissolved when the moving average trendline crossed the dissolved state line. Moving average crossing dissolved state line is illustrated in **Figure 5.2.1**. In some measurements standard deviation values started to increase again after a time and in these cases the dissolved state line was drawn to the level where standard deviation values were at their lowest.

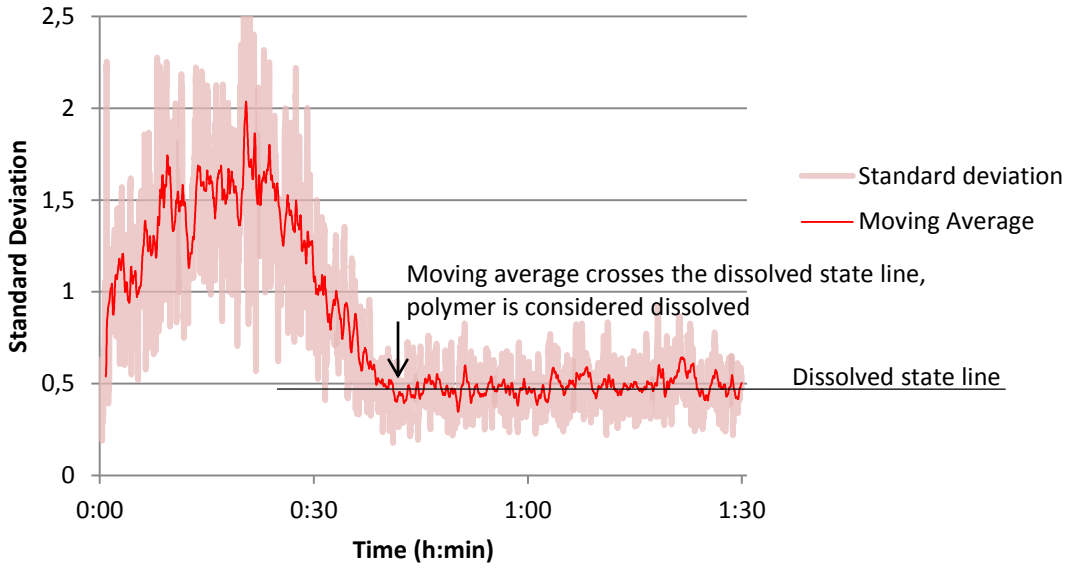


Figure 5.2.1 Determining the dissolution time from standard deviation results.

The results from optical measuring system measurements with room temperature DI H_2O as a solvent are first presented. The standard deviation results can be seen in **Figure 5.2.2** and the averages describing turbidity level in **Figure 5.2.3**.

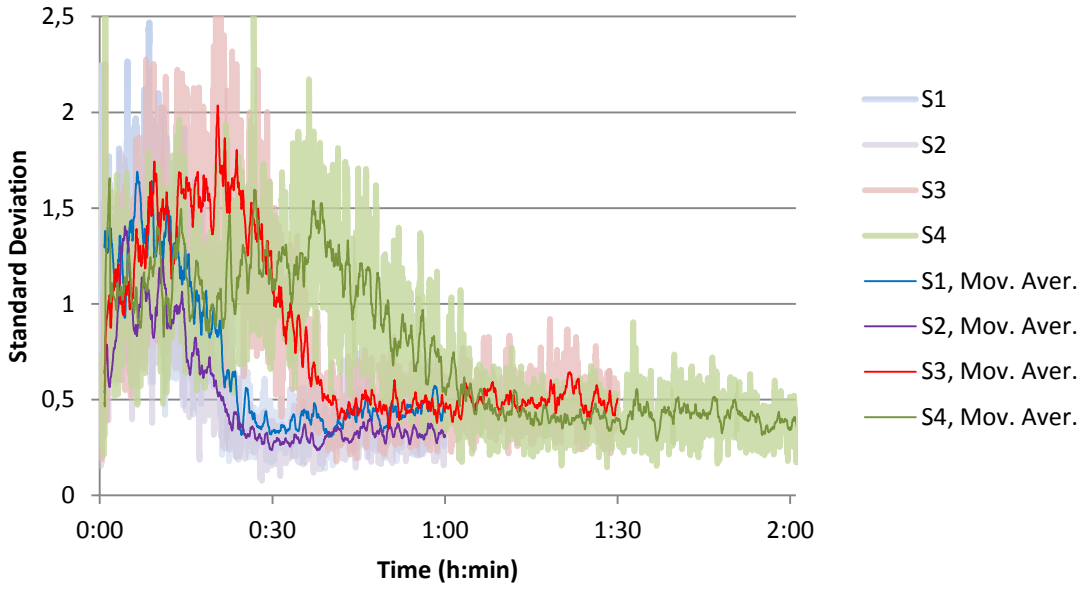


Figure 5.2.2 Standard deviation results from measurements with room temperature DI H_2O as a solvent.

As can be seen from the Figure 5.2.2, the samples with different dissolution rates are relatively easy to distinguish. The standard deviation values of the fast dissolving samples S1 and S2 stabilize faster than the other two (S3 and S4). For the slowest dissolving sample S4 the values stabilize last.

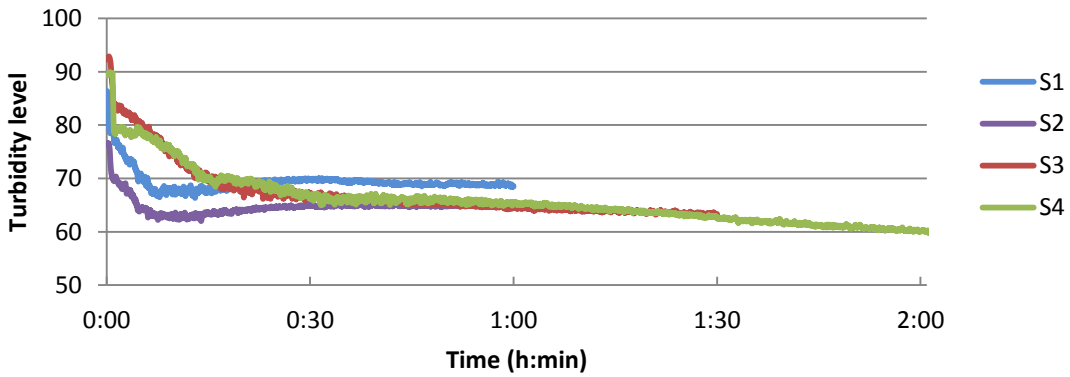


Figure 5.2.3 Averages from measurements with room temperature DI H_2O as a solvent.

The turbidity levels in Figure 5.2.3 are quite similar to each other. During the first 10 to 15 minutes the turbidity levels decreased significantly, but after that the changes were slower. For the fast dissolving samples S1 and S2, the turbidity increases slightly after the beginning, whereas the turbidity of the samples S3 and S4 continues to decrease. As the standard deviation changes were used instead of turbidity level changes in determining the dissolution rates, the turbidity levels are not discussed further.

As mentioned in Section 5.1, the sensitivity of the method was tested by changing some of the parameters affecting the dissolution rate. Results from these measurements are presented next. First the results with **different solvents** are shown, and then the measurements with different solvent temperatures in the beginning. The obtained dissolution times for comparing DI H_2O, tap water and 0.05M NaCl in DI H_2O as a solvent can be seen in **Figure 5.2.4**.

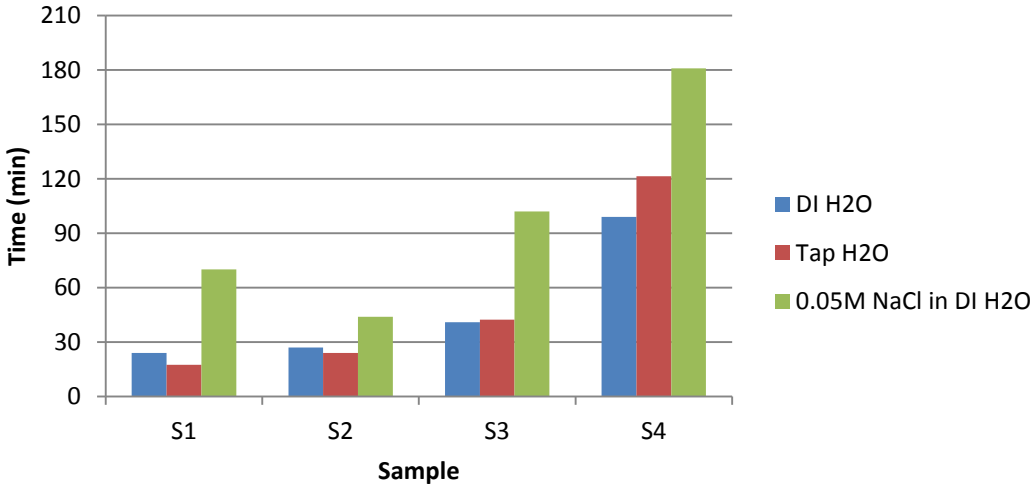


Figure 5.2.4 Obtained dissolution times from measurements with different solvents (DI H_2O, tap water and 0.05M NaCl in DI H_2O) at room temperature.

When tap water was used as a solvent instead of DI H_2O, the dissolution times did not change remarkably. For the high charge level samples S1 and S2 the dissolution rate decreased some and for the samples with lower charges (S3 and S4) the dissolution

required a bit more time. However, the changes were modest especially when compared to the salt containing solvent. When 0.05M NaCl in DI H_2O was used, the dissolution rates decreased significantly for each sample.

Results from measurements with **different temperature** DI H_2O as a solvent are presented next. The cold solvent was approximately 6–8 °C and the warm 40–41 °C in the beginning of the measurement. It should be noted that as the measurements were performed at room temperature (rt), the solvent temperatures changed during the dissolution. The cold solvent warmed approximately 9 °C per hour. The obtained dissolution times for the cold solvent can be seen in **Figure 5.2.5**.

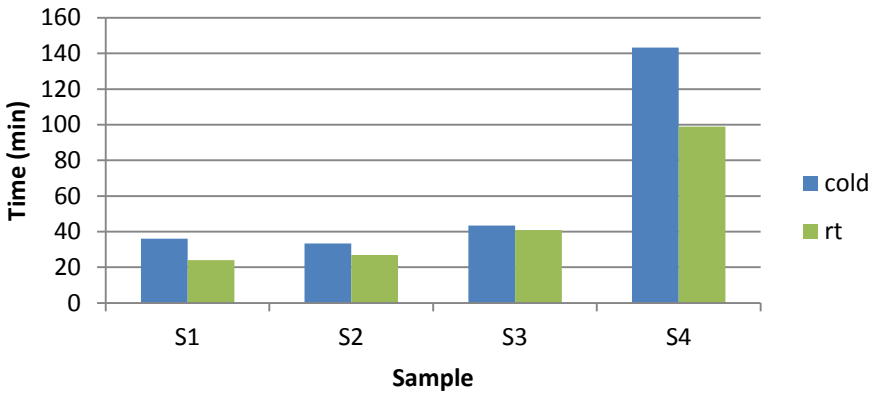


Figure 5.2.5 Obtained dissolution times from measurements with different solvent temperatures in the beginning and a stirring speed of 350 rpm.

Cold temperatures gave slightly longer dissolution times for the samples S1, S2 and S3. For the sample S4, the difference was greater as the dissolution time increased approximately by 40 minutes.

With warm solvent, the standard deviation figures were quite different compared to other measurements. For comparison, the standard deviation results for the sample S1 with different solvent temperatures are presented in **Figure 5.2.6**.

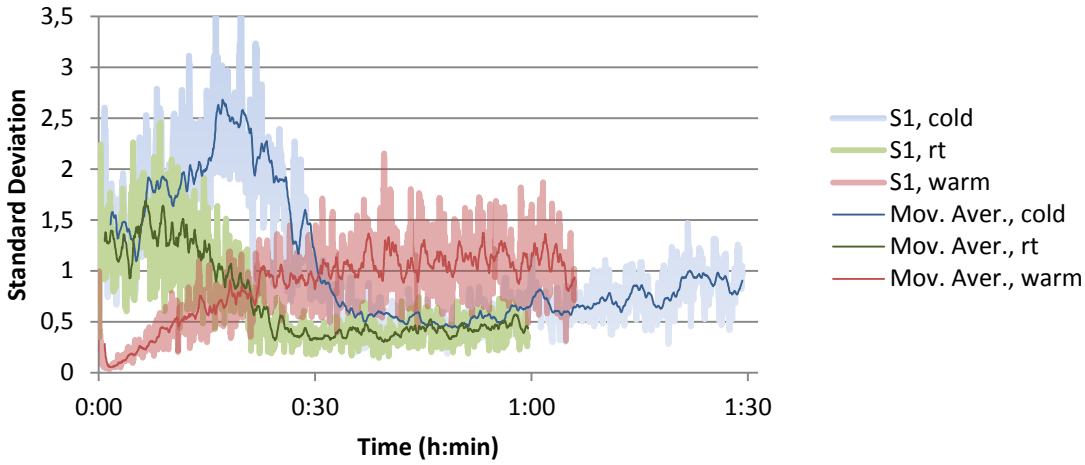


Figure 5.2.6 Standard deviation results for the sample S1 from measurements with different solvent temperatures in the beginning.

The standard deviation values stabilized slower with the cold solvent than with the room temperature solvent. The shapes of these curves were similar to each other, whereas the measurement with warm solvent gave rather different results. With warm solvent, the standard deviation was low at first and then started to increase. Similar results were obtained with the other samples as well.

The standard deviation results from the measurements with warm solvent for all samples can be seen in **Figure 5.2.7**. As the standard deviation values seemed not to give accurate information about the dissolution of PAM, the dissolution times could not be determined.

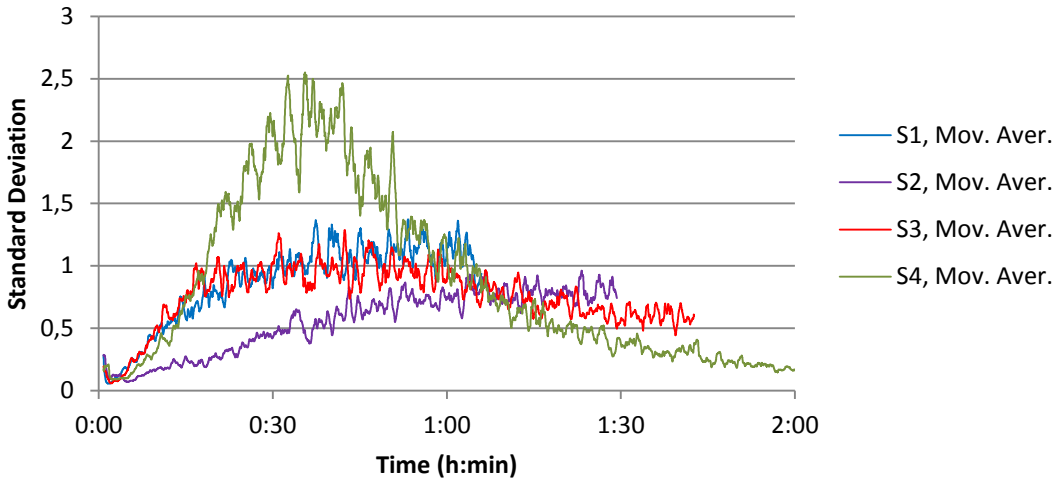


Figure 5.2.7 Standard deviation results from measurements with warm DI H_2O as a solvent and a stirring speed of 350 rpm.

Next, the effect on **stirring speed** was tested. In the measurement procedure after 1 min the stirring speed was decreased to 350 rpm. Therefore, tests with stirring speeds of 250 and 450 rpm were made for comparison. The results can be seen in **Figure 5.2.8**.

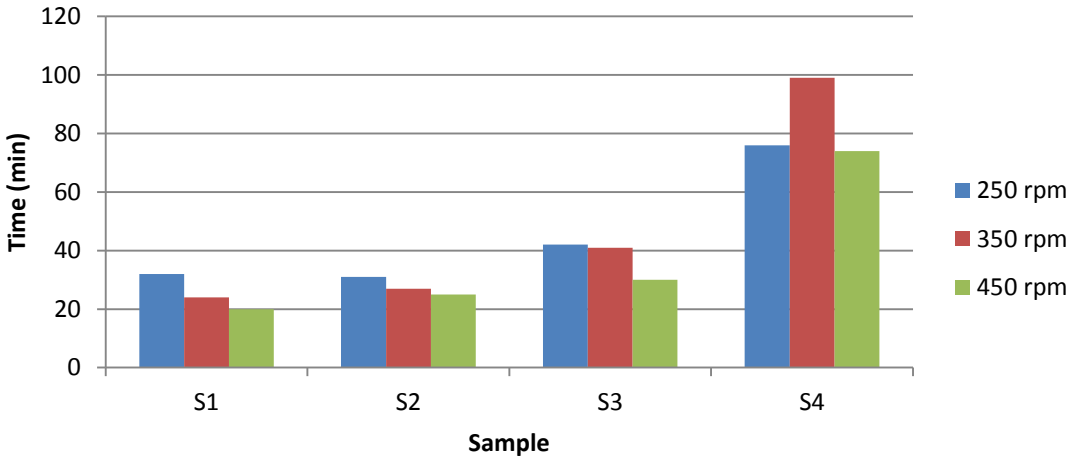


Figure 5.2.8 Obtained dissolution times from measurements with different stirring speeds (250, 350 and 450 rpm) after 1 min and room temperature DI H_2O as a solvent.

As can be seen, decreasing the stirring speed decreases the dissolution rate, at least for the samples S1, S2 and S3. For the slow dissolving sample S4 the standard deviation curves decrease in a logical order as the decrease is faster with increasing stirring speed. However, even in the stabilized level the standard deviation values are fluctuating quite a lot for the sample S4. This standard deviation fluctuation can cause inaccuracy when determining the dissolution times and might explain the dissolution time differences for the sample S4.

The results from the **particle size tests** are then presented. The sample S1 was run through a 500 µm sieve and the different fractions were collected. The measurement was then done with the different fractions according to the procedure described in Section 5.1.1. The standard deviation changes during the measurement can be seen in **Figure 5.2.9**.

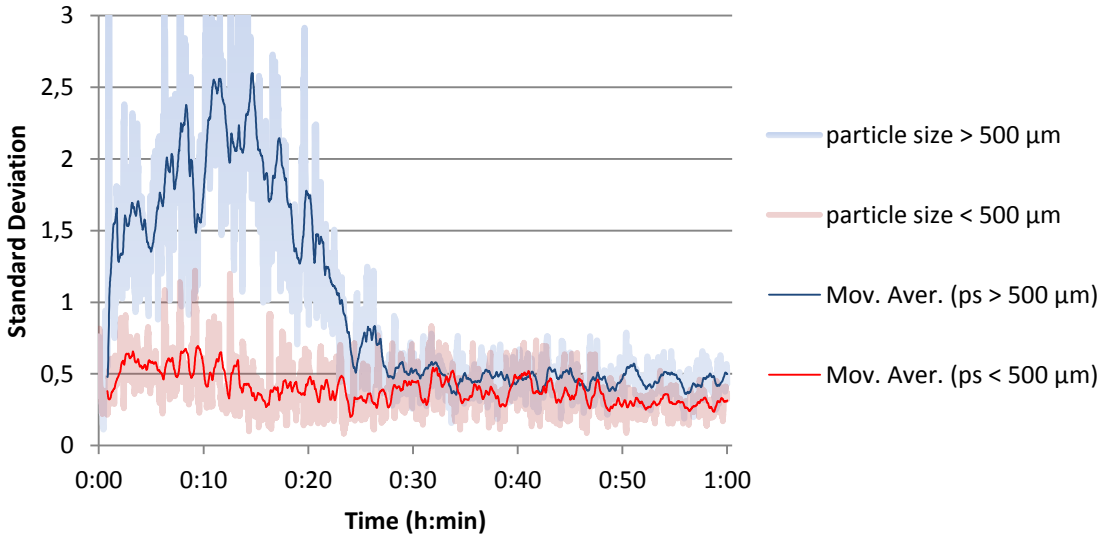


Figure 5.2.9 Standard deviations results from particle size test with sample S1.

As can be seen from the figure, the method is extremely sensitive to particle size differences. If the solute particle size is small enough, the standard deviation stays small

throughout the dissolution, which increases the inaccuracy of assessing the dissolution rate. For the sample S1 smaller solute particle size let to dissolution time of less than 15 minutes, which is less than half of the dissolution time obtained with the bigger particle size.

Furthermore, it was observed that smaller solute particle size left the turbidity level of the prepared solution higher. The averages describing turbidity level can be seen in **Figure 5.2.10**. The turbidity level obtained with bigger particles was less than 75% of the level obtained with the smaller particles.

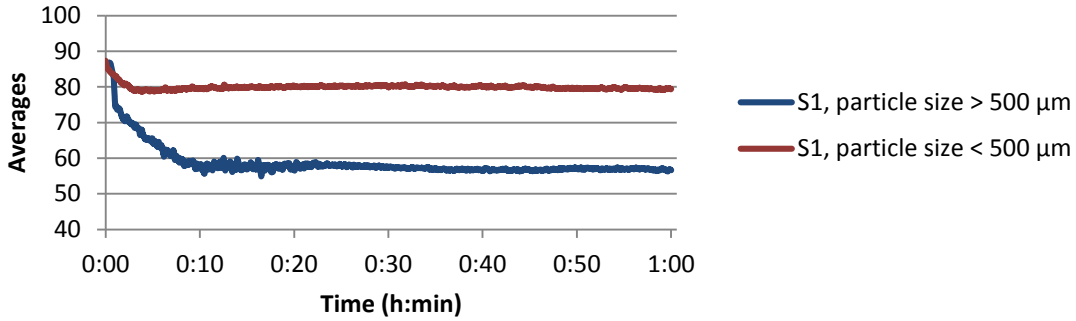


Figure 5.2.10 Averages from particle size test with sample S1.

5.3 Measurements with a torque stirrer

5.3.1 Procedure

The procedure for the torque stirrer measurements was chosen so that it was similar to the procedure of the quality control method QCTM35 performed in Kemira. Therefore, the used volume was more than triple amount compared to the other measurement methods and the concentration was slightly different from 5 wt%. In the torque stirrer measurements the amount of PAM was 0.5wt% of the amount of solvent instead of the total mass of the solution, which gives a concentration of 0.498 wt%. Nevertheless, as the concentration is so small that the difference is insignificant.

First the conductivity and temperature of the solvent were measured with a conductivity meter. Then 1500g ± 0.02g of solvent was measured into a 2000 ml beaker. The beaker was placed under the torque stirrer and the stirrer blade (described in Section 4.2) was placed approximately 1 cm off bottom. Stirring was set to 370 rpm in order to form a proper vortex. 7.50 g ± 0.01 g of cationic PAM was sprinkled to the edge of the generated vortex in approximately 7 seconds. After the addition data collection was started and the solution mixture was stirred for 2 min.

After 2 min the stirring was decreased to 300 rpm. The time of measurement depended on the sample as mentioned in the beginning of Chapter 5. When the polymer was dissolved completely, data collection was stopped and the obtained data was saved.

5.3.2 Results

Averages were calculated for the obtained values and moving average trendlines of 50 values were drawn with Microsoft Excel. The calculations were done similarly to the optical measurement calculations described in Section 5.2.2.

The polymer was considered dissolved when the moving average reached its maximum. The torque averages from torque stirrer measurements with room temperature DI H_2O as a solvent can be seen in **Figure 5.3.1**.

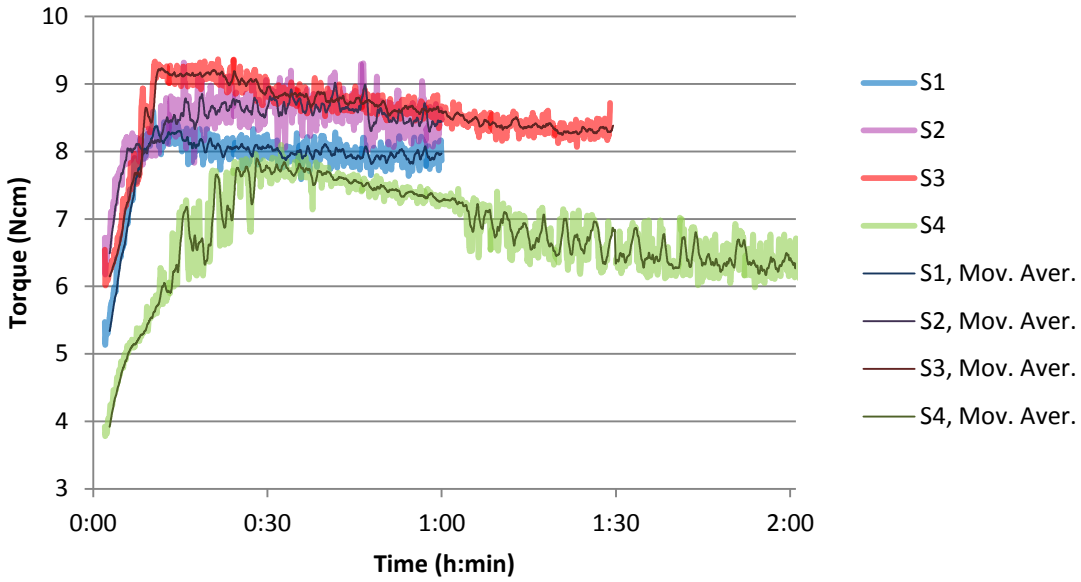


Figure 5.3.1 Torque averages from torque measurements with room temperature DI H_2O as a solvent and a stirring speed of 300 rpm.

From the figure it can be seen that the samples S1 and S3 reached their maximum torques first. The samples S4 and S2 required approximately twice as much time to reach their maximum torques. Even though the defined dissolution time of the sample S4 is four times the defined dissolution time of the sample S2, sample S4 reaches its maximum torque a bit before the sample S2.

All the samples reach their maximum torque in less than 40 minutes. These obtained dissolution times are remarkably shorter than the defined dissolution times. For the samples S1, S3 and S4 the torque first increases and right after reaching the maximum, the torque starts to decrease slowly. Therefore, the maximum torque is easily determined.

For the sample S2 the torque values even out after the first, fast increase. Therefore, even though a certain torque level is reached quite fast with the sample S2, the maximum torque itself can be observed much later as the torque values fluctuate. For this reason, the maximum torque might not be the best choice for assessing the

dissolved state of the sample S2. For example 90% of the maximum torque could be considered as the point when the polymer is dissolved. Then the obtained dissolution times for the sample S2 would be quite different. This observation is discussed more in Chapter 6.

The sensitivity of the method was tested by changing different parameters affecting dissolution rate. Results from these measurements are presented next. First the results comparing **different solvents** are shown, and then the measurements with different solvent temperatures in the beginning. The results from the measurements with DI H_2O, tap water and 0.05M NaCl in DI H_2O as solvent can be seen in **Figure 5.3.2**.

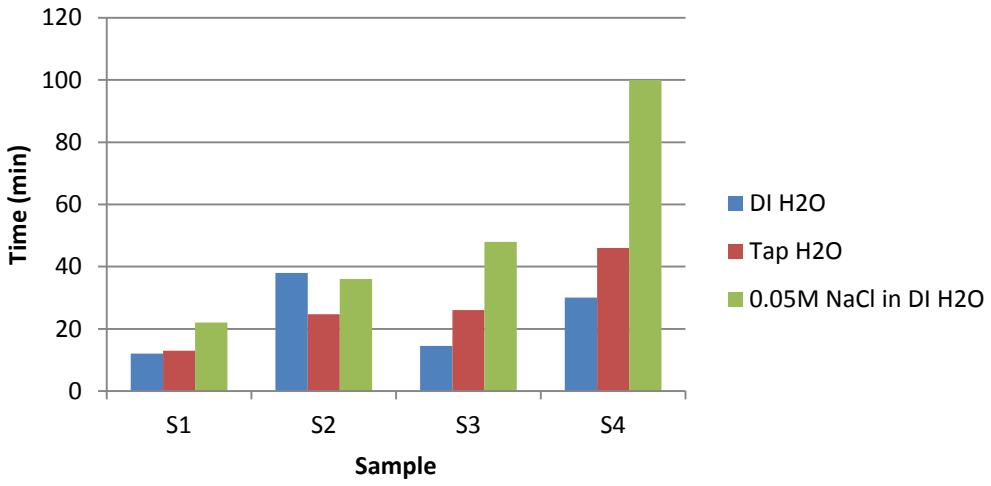


Figure 5.3.2 Obtained dissolution times from torque measurements with different solvents (DI H_2O, tap water and 0.05M NaCl in DI H_2O) at room temperature and a stirring speed of 300 rpm.

For samples S1, S3 and S4 the dissolution required a bit more time when tap water was used as a solvent, but the difference was clearer with the lower charge level samples S3 and S4. When 0.05M NaCl in H_2O was used, the dissolution required even more time. As with tap water, the difference was greater with the low charge level polymers.

For the very high molecular weight and very high charge level sample S2 the results are quite different. The obtained dissolution times with DI H_2O and 0.05 M NaCl in DI H_2O are similar to each other, but the dissolution time with tap water is surprisingly lower than the other two. These differences might result from the fluctuating torque values of the sample S2 as explained earlier in this section.

The dissolution times for **different temperature** DI H_2O as a solvent can be seen in **Figure 5.3.3**. The cold solvent was approximately 6–7 °C and the warm 39–41 °C in the beginning of the measurement. It should be noted that as the measurements were performed at room temperature, the solvent temperatures changed during the dissolution. The cold solvent warmed approximately 5 °C per hour.

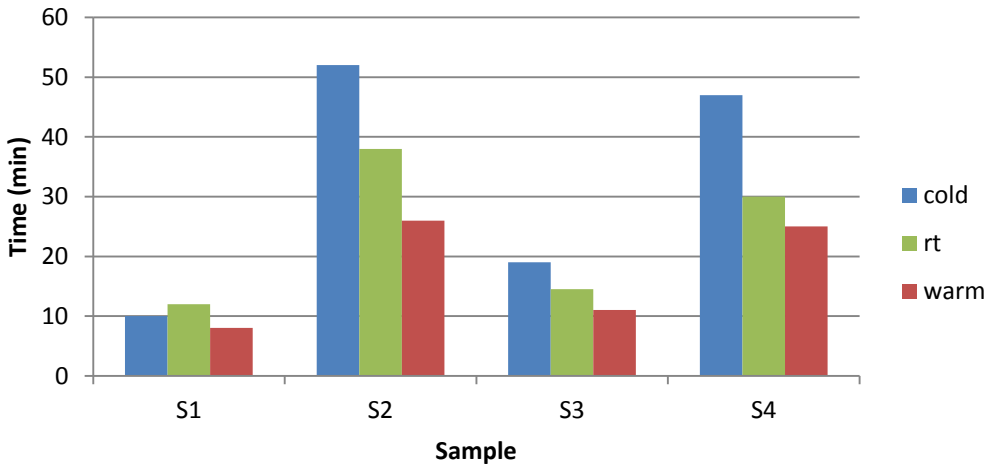


Figure 5.3.3 Obtained dissolution times from torque measurements with different solvent temperatures in the beginning and a stirring speed of 300 rpm.

As can be seen, generally the dissolution rate increases with increasing temperature. However, for the sample S1 the cold solvent gave slightly shorter dissolution time than the room temperature solvent. Nevertheless, all the dissolution times for the sample S1 are very similar to each other despite the solvent temperature.

For the other samples S2, S3 and S4, the differences are greater. It should be noted that longer dissolution times are obtained for the fast dissolving sample S2 than for the slow dissolving sample S4.

Next, the effect on **stirring speed** was tested. In the measurement procedure after 2 min the stirring speed was decreased to 300 rpm. Therefore, tests with stirring speeds of 200 and 400 rpm were made for comparison. The obtained dissolution times can be seen in **Figure 5.3.4**. The effect of stirring speed to the dissolution times cannot be clearly seen with this method as the results for the different samples are not similar to each other.

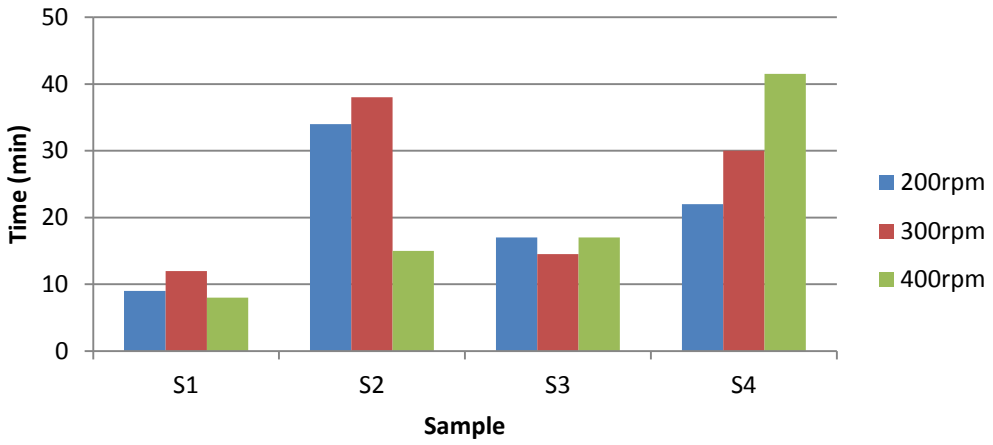


Figure 5.3.4 Obtained dissolution times from torque measurements with different stirring speeds after 2 min and room temperature DI H_2O as a solvent.

In the stirring speed tests it was noticed that the torque levels are remarkably different with different stirring speeds. The torque level increases with increasing stirring speed. In the **Figure 5.3.5** the torque averages of sample S2 are presented as an example. The same phenomenon was observed with all samples.

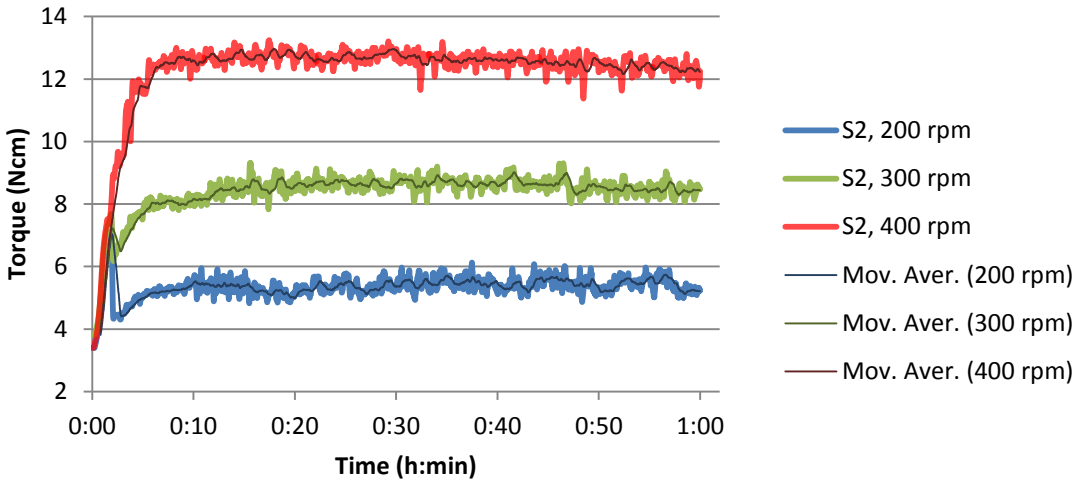


Figure 5.3.5 Averages from measurements with different stirring speeds for the sample S2.

In the **particle size test**, sample S1 was run through a 500 µm sieve and the different fractions were collected. The measurement was done with the different fractions according to the procedure described in Section 5.3.1 and the results are presented in **Figure 5.3.6**.

With small particles (particle size < 500 µm) the maximum torque was reached in 4 minutes, whereas the time for bigger particles was 12 minutes. As the obtained dissolution time for the bigger particle size was three times longer, the method is clearly sensitive to particle size differences.

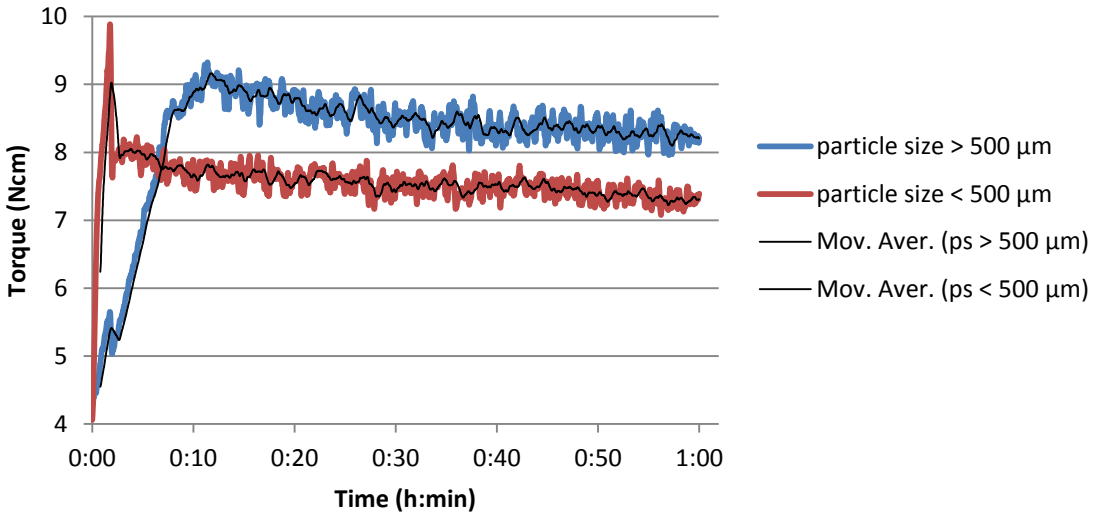


Figure 5.3.6 Torque averages from particle size test with the sample S1.

5.4 Measurements with a rotational viscometer

5.4.1 Procedure

First the conductivity and temperature of the solvent were measured with a conductivity meter. Then 400.00 g ± 0.01 g of solvent was measured into a 600 ml beaker and a magnet (thick, high viscosity specific) was added for stirring. The beaker was placed under the viscometer. Stirring was set to 550 rpm in order to form a proper vortex. 2.000 g ± 0.001 g of cationic PAM was sprinkled to the edge of the generated vortex in approximately 6 seconds. After the addition data collection was started and the solution mixture was stirred for 1 min.

After 1 min the stirring was decreased to 350 rpm and the spindle was put into the solution. The time of measurement depended on the sample as mentioned in the beginning of the Chapter 5. Before ending the measurement the solution was observed for insoluble particles. If insoluble particles were observed, the measurement was continued. When the polymer was dissolved completely, the data collection was stopped and the obtained data was saved.

It should be noted that spindles and the rotating speed of the spindles differed in different measurements as the viscosities obtained with the different samples are also different. Therefore, even though the results of several measurements are presented in the same figure, the results should not be compared with each other without this in mind. The spindles were chosen so that the limit of the measurement range would correspond to the maximum viscosity of the sample. The used spindles were RV2 and RV3 and the rotating speeds of the spindles were 50 and 100 rpm.

5.4.2 Results

Averages were calculated for the obtained values and moving average trendlines of 50 values were drawn with Microsoft Excel. The calculations were done similarly to the optical measurement calculations described in Section 5.2.2.

The polymer was considered dissolved when the moving average reached its maximum. The results from viscometer measurements with room temperature DI H_2O as a solvent

can be seen in **Figure 5.4.1**. These measurements were done with spindle RV3 and the rotating speed of the spindle was 100 rpm, which gave a measurement range from 1 to 1000 mPas. Therefore, in principle the results can be compared with each other, but it should be noted that the measurement range is not optimal for all of the samples. For example the maximum viscosity of the sample S4 is only 40% of the whole measurement scale.

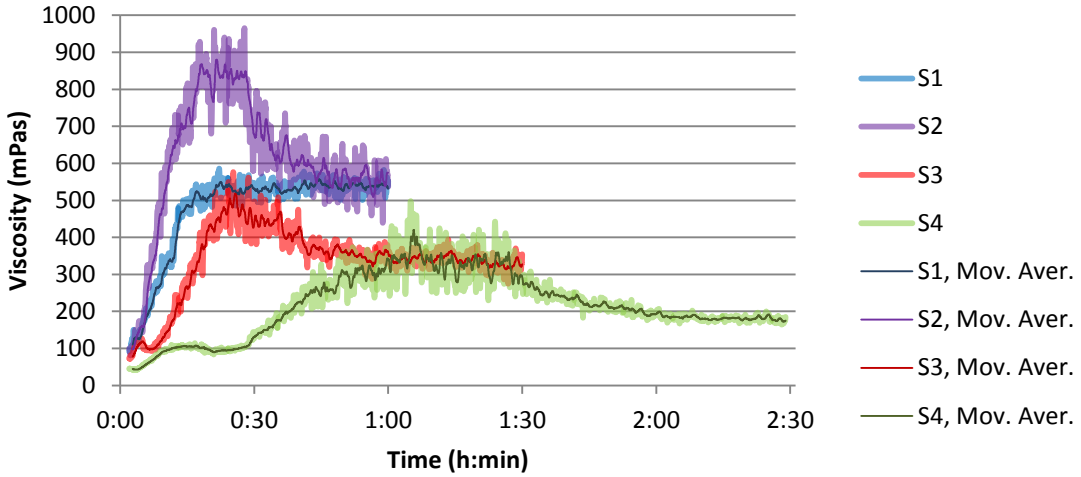


Figure 5.4.1 Viscosity averages from measurements with room temperature DI H_2O as a solvent and spindle RV3 with rotating speed of 100 rpm.

From the figure it can be seen, that in the beginning of the dissolution the viscosities of the fast dissolving samples S1 and S2 increase faster than the viscosities of the slow dissolving samples S3 and S4. The slowest dissolving sample S4 reaches its maximum viscosity much later than the other samples. In contrast, the sample S3 reaches its maximum viscosity almost at the same time as S1, even though these samples have different defined dissolution times.

Interestingly, it is observed that the viscosities of S2, S3 and S4 first increase to their maximum, but then their viscosities decrease a great deal. After a while the viscosity values stabilize. If these stabilized viscosity levels would determine the dissolution time

instead of the maximum viscosities, the results would be quite different and this observation is discussed more in the Chapter 6.

The sensitivity of the method was tested by changing different parameters affecting dissolution rate and results from these measurements are presented next. First the results comparing **different solvents** are shown, and then the measurements with different solvent temperatures in the beginning. The results from the measurements with DI H_2O, tap water and 0.05M NaCl in DI H_2O as solvent can be seen in **Figure 5.4.2**.

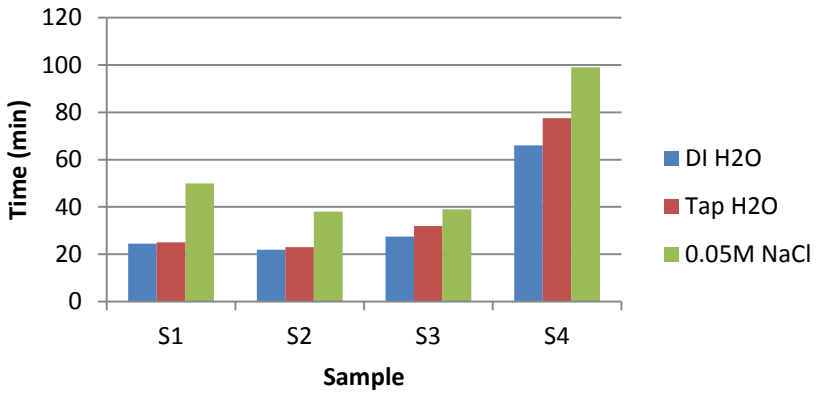


Figure 5.4.2 Obtained dissolution times from measurements with different solvents (DI H_2O, tap water and 0.05M NaCl in DI H_2O) at room temperature and a stirring speed of 350 rpm.

When tap water was used as a solvent instead of DI H_2O, the dissolution times did not change significantly. For the samples S2, S3 and S4 the dissolution times were a little longer. With 0.05M NaCl DI H_2O as the solvent, the dissolution required even more time. However, for the sample S1 the dissolution time was not as easy to determine as for the others as the viscosity first increased, then decreased and increased again. The first viscosity maximum was observed already after 11 minutes.

The dissolution times for **different temperature** DI H_2O as a solvent can be seen in **Figure 5.4.3**. The cold solvent was approximately 6–7 °C and the warm 40–42 °C in the

beginning of the measurement. It should be noted that as the measurements were performed at room temperature, the solvent temperatures changed during the dissolution. The cold solvent warmed approximately 9 °C per hour.

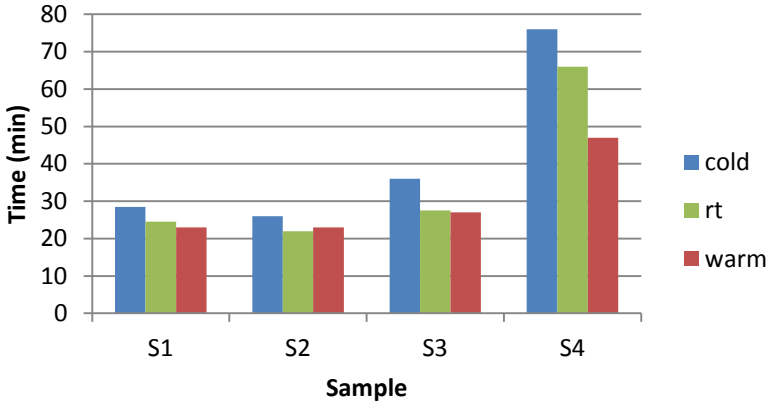


Figure 5.4.3 Obtained dissolution times from measurements with different solvent temperatures in the beginning and a stirring speed of 350 rpm.

In general, the dissolution rate increases with increasing temperature. However, the differences in the obtained dissolution times especially with room temperature and warm solvent for samples S1, S2 and S3 are minor. The biggest differences can be seen in the results of the slow dissolving sample S4.

Next, the effect on **stirring speed** was tested. In the measurement procedure after 1 min the stirring speed was decreased to 350 rpm. Therefore, tests with stirring speeds of 250 and 450 rpm were made for comparison. The obtained dissolution times can be seen in **Figure 5.4.4**.

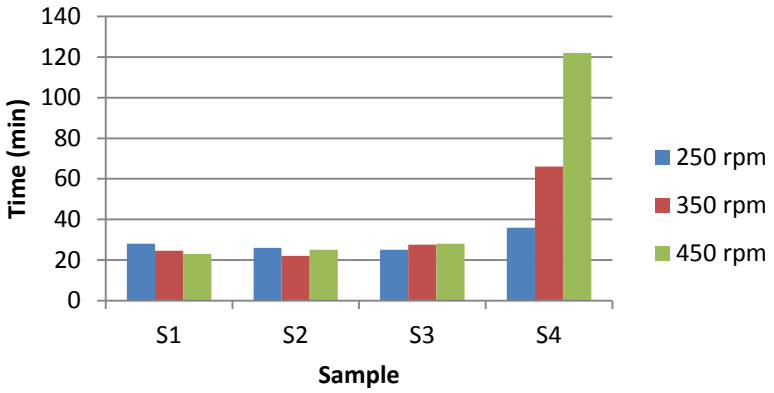


Figure 5.4.4 Obtained dissolution times from measurements with different stirring speeds after 2 min and room temperature DI H_2O as a solvent.

For the samples S1, S2 and S3 the stirring speed seem not to have a significant effect on the dissolution rate. The results for the sample S4 were unexpected as instead of decreasing, the dissolution time increased with increasing stirring speed. However, as the figures from these measurements were quite different compared to each other, some additional measurements would be in order to avoid hasty conclusions.

In the **particle size test**, sample S1 was run through a 500 µm sieve and the different fractions were collected. The measurement was done with the different fractions according to the procedure described in Section 5.4.1 and the results can be seen in **Figure 5.4.5**.

With small particles (particle size < 500 µm) the viscosity started to increase approximately 4 minutes faster than with the bigger particles. However, in the measurements with smaller particles, the polymer addition was not successful as some of the polymer agglomerated into one insoluble agglomeration each time. Therefore, even though it seems that the particle size does not have that much effect on the method further experiments are needed to be certain.

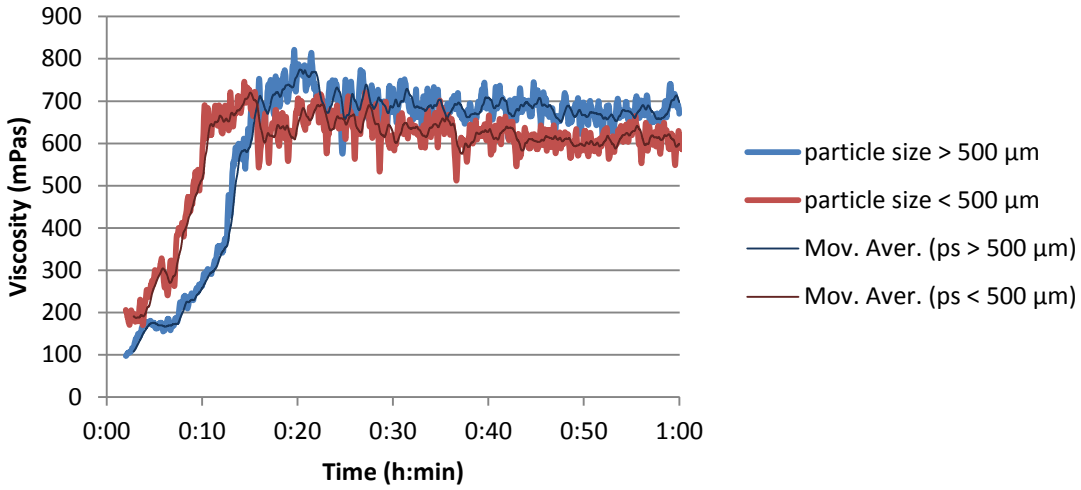


Figure 5.4.5 Viscosity averages from particle size test with sample S1.

6 Inspection of the research results

In this chapter the results presented in Chapter 5 are discussed further and reviewed one method at a time. The methods are then compared with each other in Section 6.4.

6.1 Optical measurement system

The obtained dissolution times with optical measuring system corresponded to the defined dissolution times quite accurately. For the fast dissolving samples S1 and S2 the results were corresponding to the defined values exactly as for the slower dissolving samples S3 and S4 the obtained dissolution times were a bit shorter than the defined times.

The dissolution rates for the different samples were relatively easy to distinguish from each other especially in the beginning of the dissolution when the dissolution rate was high. However, the end of the dissolution was in some cases more complicated to assess. In some measurements the standard deviation values fluctuated remarkably and in some cases the standard deviation started to increase again after a time. In these situations, determining the dissolution time with drawing the dissolved state line can give inaccurate results, as the moving average can cross the dissolved state line before the sample has truly dissolved.

Furthermore, during the measurement only the turbidity levels can be monitored and sometimes the turbidity levels seem to even out already during the ongoing dissolution. This might result with a too short measurement time, if the defined dissolution times are not known.

The last undissolved transparent particles in the very end of the dissolution were relatively easy to observe ocularly, but the method itself is not sensitive enough to observe them.

In the parameter tests, most of the results were as expected. Adding salt to the solvent slowed the dissolution rate as well as using cold solvent. However, with tap water the differences in the dissolution rates were minor.

Using warm solvent resulted with surprising results. With all samples, the standard deviation was small already in the beginning of the dissolution and approximately after five minutes the standard deviation started to increase. Because of the strange shape of the standard deviation figures, the dissolution times could not be determined from the results.

Optical measuring system showed that increasing the stirring speed increased the dissolution rate, but the changes were relatively small. The slow dissolving sample S4 gave divergent results when considering the obtained dissolution times, but from the standard deviation figures it could be seen that the standard deviation decreased faster with increasing stirring speed. The divergent dissolution times with the sample S4 show that the fluctuating standard deviation can result with inaccurate dissolution times.

The optical measuring system was extremely sensitive to particle size differences. When the particle size was small (particle size < 500 µm), the standard deviation stayed small throughout the dissolution, which made assessing the dissolution rate difficult. With the small particles, the obtained dissolution time was less than half of the time with the bigger particles. Because of the significant effect that the particle size has to the results, it should be made sure that the samples used with optical measurement system do not contain any polymer dust residues that will affect the results.

6.2 Torque stirrer

The obtained dissolution times by determining maximum torques of the solutions corresponded poorly to the defined dissolution times. All of the samples reached their maximum torques in less than 40 minutes. Furthermore, the fast and slow dissolving samples were hard to distinguish from each other. The fast dissolving sample S1 reached its maximum torque approximately at the same time as slow dissolving sample S3, whereas the torque of the other fast dissolving sample S2 first increased the fastest but after five minutes the torque increase slowed down. Also the very slowly dissolving sample S4 reached its maximum torque already in 30 minutes.

For the samples S1, S3 and S4 the torque first increased and right after reaching the maximum, the torque started to decrease slowly. Therefore, the maximum torque was

easily determined. For the sample S2 the torque evened out after the first, fast increase in torque instead of decreasing. Therefore, even though a certain torque level was reached quite fast with the sample S2, the maximum torque itself was observed much later as the torque values fluctuated. This made assessing the dissolution time from the maximum torque quite inaccurate for the sample S2. It is also the reason why the sample S2 has the longest dissolution times in the torque measurements.

Nevertheless, another way for assessing the dissolution time could be used. If for example 90% of the maximum torque would be considered as the point when polymer is dissolved, the results would be quite different for the sample S2. The difference can be clearly seen when the time of reaching the maximum torque is compared to the time when 90% of the maximum viscosity is achieved. This comparison is presented in **Figure 6.2.1**.

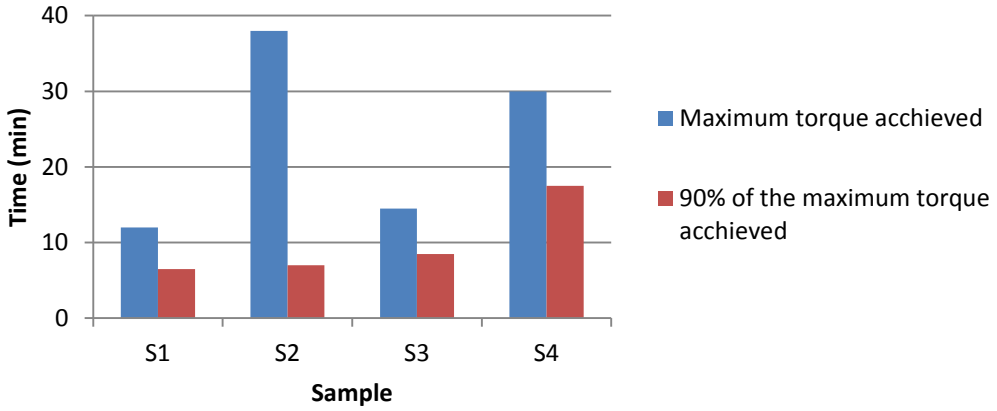


Figure 6.2.1 Time when maximum torque is observed compared to the time when 90% of the maximum torque is achieved, torque measurements with room temperature DI H_2O as a solvent and with a stirring speed of 300 rpm.

For the samples S1, S3 and S4, the time when 90% of the maximum is achieved is approximately 57% of the time when maximum torque is achieved. However, the same value for the sample S2 is only 18%. From these results is can be seen, that the obtained

time for the sample S2 is much longer compared to the other samples, when maximum torque is considered as the dissolved state. When 90% of the maximum torque was used to determine the dissolved state, the fast dissolving samples S1 and S2 reached the value in the same time, as they should as their defined dissolution times are the same. However, defining the dissolved state with a percentage value gives even shorter dissolution times.

From the different parameter tests, some observations were made. When different solvents were tested, the greatest differences were observed with the samples with lower charges. The lower charged samples S3 and especially S4 had much slower dissolution rates when salt was added to the solvent. For the samples S3 and S4, the obtained dissolution times with 0.05M NaCl in DI H_2O as the solvent were more than one and a half times the dissolution time obtained with DI H_2O as the solvent.

In the temperature tests, the dissolution rate increased with increasing temperature. The dissolution time was approximately 26% shorter when warm solvent was used instead of room temperature and 42% longer with cold solvent. Only for the sample S1 the dissolution time was slightly shorter with the cold solvent than the room temperature solvent, but it should be noted that all the obtained dissolution times for sample S1 were very similar to each other.

When the effect of stirring speed was tested, it was noticed that the dissolution rates in the beginning were increasing with increasing stirring speed. The obtained torque levels were also different according to the stirring speed. With the highest stirring speed (400 rpm) the torque levels were at least twice as high as with the lowest stirring speed (200 rpm) for each sample.

However, when considering the maximum torques the results are much more varying. For example the slow dissolving sample S4 reached its maximum torque later with increasing stirring speed. In contrast, the maximum torque for the sample S2 was reached much sooner with the highest stirring speed than the other stirring speeds. For the samples S1 and S3 the differences were minor. From these observations it can be

concluded that the obtained dissolution times are affected by the stirring speed changes in different ways and this can lead to inaccurate results.

In the particle size tests the dissolution rate differences were clearly seen with the torque stirrer. With small particles (particle size < 500 µm) the maximum torque was reached three times faster than with the bigger particles.

With torque stirrer the dissolution rates for the different samples can only be observed in the beginning of the dissolution. Even then the samples with small differences in dissolution time, such as samples S1 and S3, cannot be distinguished from each other. For the reasons explained above, the dissolution rate of PAM cannot be accurately assessed with a torque stirrer.

6.3 Rotational viscometer

If a polymer sample is considered dissolved as the solution mixture reaches its maximum viscosity, the obtained dissolution times for the fast dissolving samples S1 and S2 are a bit shorter than the defined dissolution times. Furthermore, the obtained values for the slower dissolving samples S3 and S4 are only approximately half of the defined dissolution times.

Also another approach is possible. After the viscosity has reached its maximum, with samples S2, S3 and S4 the viscosity then decreases and finally stabilizes. If the stabilized viscosity level would be considered as the dissolved state, the results would be quite different. Therefore, similarly to determining the dissolution time from optical measuring system measurements (described in Section 5.2.2), straight line was drawn to the stabilized viscosity level and the time when the moving average crossed the line was recorded. The comparison between the defined dissolution times, times when maximum viscosity is reached and the time for moving average crossing the stabilized viscosity level can be seen in **Figure 6.3.1.**

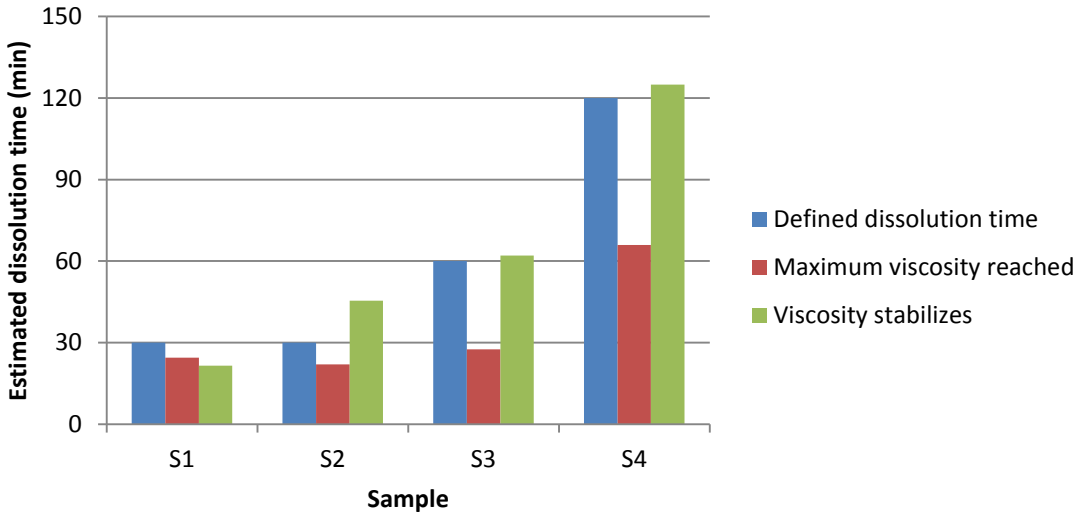


Figure 6.3.1 Comparison between defined dissolution times and dissolution times from viscosity measurements.

It can be clearly seen that the stabilized viscosity levels correspond to the defined dissolution times better than the times for maximum viscosities when the lower charge polymer samples S3 and S4 are considered. For the high level charge sample S1 there is not a much difference, as the viscosity stays approximately in the same level after reaching the maximum viscosity. However, the very high molecular weight sample S2 which has the same charge level as S1 results with twice as long dissolution time when the stabilized level is considered as the dissolved state.

The decrease in viscosities with the samples S2, S3 and S4 might be due their very high molecular weight level. The viscosity of the sample S1 did not decrease after reaching its maximum, whereas the viscosities of all the very high molecular weight level samples (S2, S3 and S4) decreased after reaching their maximum. As the solution mixture is stirred and the spindle rotates in the solution, shear forces are generated that might cause the long polymer chains to degrade. As shorter chains are formed the viscosity of the solution decreases with the decreasing molecular weight. As the sample S1 has slightly lower molecular weight than the other samples, the same phenomenon is not observed.

Another explanation could be conformational changes during the dissolution. The long polymer chains of the very high molecular weight level samples might form coils that first give an increase in the viscosity, but as the chains open, the viscosity decreases until the polymer chains have found more stabilized configurations.

Next the parameter test results are discussed. When the effects of the different parameters were considered, the dissolution times were determined from the maximum viscosities.

Using tap water as a solvent had no effect on the dissolution times of the high charge level samples S1 and S2, whereas the dissolution times of the lower charge level samples S3 and S4 were slightly longer (approximately 15%). When 0.05M NaCl in DI H_2O was used as a solvent, the dissolution times were 40 to 100% longer. It should be noted, that the added salt in the solvent decreased the viscosity level of the prepared solution. Therefore, to reliably cover the viscosity range during the dissolution, different spindles and spindle speeds had to be used for the measurements.

Using cold solvent gave 5 to 10 minutes longer dissolution times than the room temperature solvent whereas the warm solvent gave quite similar results as the room temperature solvent. Only with the very lowly charged sample S4 the warm solvent speeded up the dissolution by 20 minutes.

The different stirring speeds did not have a significant effect on the observed dissolution rates, except for the sample S4. The obtained viscosity figures for the sample S4 were not similar with each other, which generates a question if the results can be reliably compared with each other. Additional measurements would be needed to assess the effect of stirring speed on the dissolution rate of the slow dissolving sample S4.

The advantage of high stirring speed is that the solution on top of the spindle mixes better. However, as the stirring speed increases, with a small volume a small vortex is formed, which might make placing the spindle more difficult. Furthermore, as the solute dissolves and the vortex dissappears due to the increase in viscosity, the spindle will be covered by the solution more than in the beginning of the dissolution.

In the particle size tests the viscosity seemed to increase couple minutes faster for the smaller particles (particle size < 500 µm). However, as the polymer additions with the smaller particles were not successful, further experiments would be needed to reliably assess the effect of the particle size.

With viscometer measurements it is possible to follow the beginning of the dissolution as the viscosities increase to their maximum levels. The slow and fast dissolving samples can be distinguished easily from their dissolution rates as the viscosities of the fast dissolving samples start to increase much faster than the slow dissolving samples.

The viscometer measurements give also additional information about the polymer solutions. The very high molecular weight level sample S2 has a more than 60% higher viscosity maximum than the little lower molecular weight sample S1. The obtained viscosity levels of the lower charge level samples are only approximately 65% (sample S3) and 40% (sample S4) of the viscosity level of the high charge level polymers S1 and S2.

If the stabilized viscosity levels are considered as the dissolved state, the dissolution times correspond quite well to the defined dissolution times. However, even though the last undissolved transparent particles in the very end of the dissolution were relatively easy to observe ocularly, the method itself is not sensitive enough to observe them. Another disadvantage of this method is that the spindles and spindle speeds have to be chosen separately for different samples. Therefore, the measurements with different samples are not directly comparable with each other.

6.4 Comparison of the different measurement methods

The dissolution rate of PAM was studied with the three different methods and the obtained dissolution times were quite different with each method. The defined dissolution times and the obtained dissolution times for the different samples are collected in the **Figure 6.4**. It should be noted that for the rotational viscometer measurements, the dissolution times were assessed from the stabilized viscosity levels as explained in the previous section.

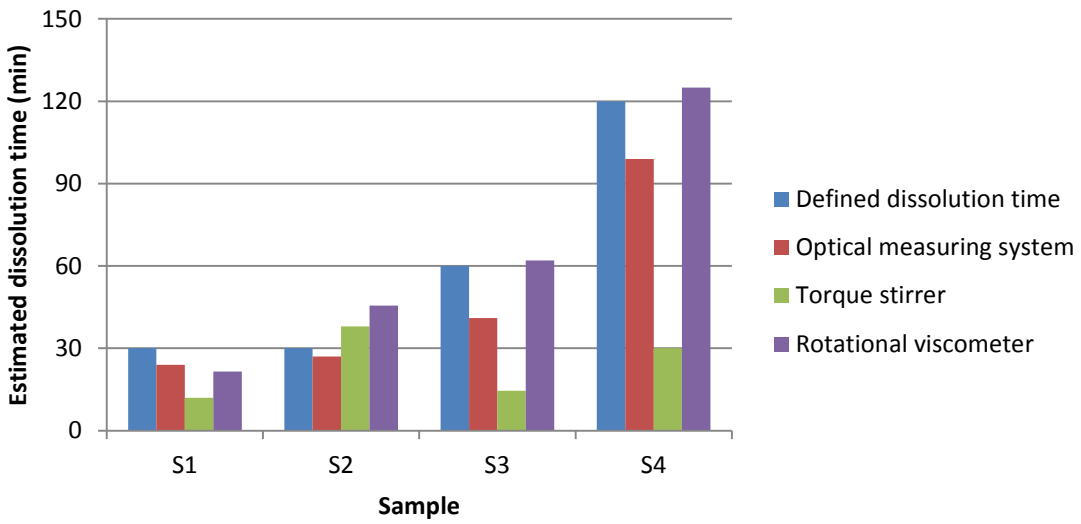


Figure 6.4 Obtained dissolution times with the different methods compared with the defined dissolution times.

As can be seen from the figure, the dissolution times obtained with optical measuring system and rotational viscometer correspond to the defined dissolution times much better than the values obtained from the torque stirrer measurements.

In torque measurements, the torque values did not stabilize as they did with the other methods, which made determining the endpoint for the dissolution difficult. Therefore, the dissolution was considered to be complete as the torque reached its maximum. However, even in the beginning of the dissolution when the torque values are increasing, the dissolution rates of the fast and slow dissolving samples cannot be clearly distinguished from each other.

In contrast, with both the optical measuring system and rotational viscometer, the dissolution rates for the different samples can be distinguished. Also as the values obtain stabilized levels in both methods, the dissolved state can be determined. However, the values from optical measuring system fluctuate more than the obtained viscosity values.

For this reason, assessing the endpoint of dissolution is more accurate with the viscometer as the repeatability is better.

Optical measuring system has one great advantage compared to the other methods. As there are no spindles or stirrer blades in the solution, the homogeneous stirring is not affected and there are no shafts for the polymer to agglomerate on. However, in theory the polymer could agglomerate into the corners of the beaker windows and affect the measurement by blocking the laser light.

Optical measuring system and torque stirrer measurements can be used similarly for all different PAM samples, but in viscometer measurements the spindles and spindle speeds have to be chosen separately for each sample. If a too broad measurement range is used, the obtained viscosity values are not reliable. Therefore, the spindle and spindle speed should be chosen so that the maximum viscosity stays just within the measurement range. This might be a problem with samples that have lower viscosities. Nevertheless, with lower viscosity samples increasing the solution concentration might help.

The biggest disadvantage of the rotational viscometer is the spindle that might cause agglomeration of the polymer. Nevertheless, LV spindles could be used instead of RV spindles as LV spindles are more commonly used for polymer solutions. LV spindles could be better for avoiding polymer agglomeration as they have smaller diameters than RV spindles.

The dissolution rate is not the only useful information obtained from the viscometer measurements. The viscosity changes during the dissolution process and the obtained viscosity level might be useful information for the applications using PAM. Conversely, the turbidity levels obtained from optical measuring system measurements or the torque values from the torque stirrer measurements are unlikely to be as useful.

Optical measuring system cannot observe the dissolution rate reliably if the particle size of the sample is too small as the standard deviation stays low throughout the

dissolution. In contrast, viscosity and torque measurements can be performed also with smaller particle size as long as the addition of the polymer sample is successful.

Furthermore, the optical measuring system measurements with warm solvent gave unusual standard deviation figures and the dissolution time could not be determined from them. With torque stirrer and rotational viscometer, the measurements were successful regardless of the solvent temperature.

From the different measurement methods, the rotational viscometer is the most accurate for determining the dissolution rate of PAM. With rotational viscometers the dissolution rates of different samples can be distinguished reliably and the endpoint for the dissolution is relatively easy to assess as the viscosity values stabilize. Furthermore, viscosity values during the dissolution and the obtained viscosity levels give additional information about the sample.

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Appendices

Appendix 1: Obtained dissolution times and their percentage values of the defined dissolution times with the list of used parameters (solvent, temperature and stirring speed).

Appendix 2: Obtained dissolution times and their percentage values of the obtained dissolution time from measurement with room temperature DI H_2O as a solvent and the list of used parameters (solvent, temperature and stirring speed).

Appendix 1: Obtained dissolution times and their percentage values of the defined dissolution times with the list of used parameters (solvent, temperature and stirring speed).

Optical measuring system												
Parameters	DI H_2O, rt, 350 rpm		Tap water, rt, 350 rpm		0.05M NaCl in DI H_2O, rt, 350 rpm		Cold DI H_2O, 350 rpm		Warm DI H_2O, 350 rpm		DI H_2O, rt, 250 rpm		DI H_2O, rt, 450 rpm	
Sample	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**
S1	24	80	18	58	70	233	36	120	-		32	107	20	67
S2	27	90	24	80	44	147	33	110	-		31	103	25	83
S3	41	68	42	71	102	170	44	73	-		42	70	30	50
S4	99	83	122	101	181	151	143	119	-		76	63	74	62
Torque stirrer														
Parameters	DI H_2O, rt, 300 rpm		Tap water, rt, 300 rpm		0.05M NaCl in DI H_2O, rt, 300 rpm		Cold DI H_2O, 300 rpm		Warm DI H_2O, 300 rpm		DI H_2O, rt, 200 rpm		DI H_2O, rt, 400 rpm	
Sample	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**
S1	12	40	13	42	22	73	10	33	8	27	9	30	8	27
S2	38	127	25	83	36	120	52	173	26	87	34	113	15	50
S3	15	24	26	43	48	80	19	32	11	18	17	28	17	28
S4	30	25	46	38	100	83	47	39	25	21	22	18	42	35
Rotational viscometer														
Parameters	DI H_2O, rt, 350 rpm		Tap water, rt, 350 rpm		0.05M NaCl in DI H_2O, rt, 350 rpm		Cold DI H_2O, 350 rpm		Warm DI H_2O, 350 rpm		DI H_2O, rt, 250 rpm		DI H_2O, rt, 450 rpm	
Sample	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**
S1	25	82	25	83	50	167	29	95	23	77	28	93	23	77
S2	22	73	23	77	38	127	26	87	23	77	26	87	25	83
S3	28	46	32	53	39	65	36	60	27	45	25	42	28	47
S4	66	55	78	65	99	83	76	63	47	39	36	30	122	102

Appendix 2: Obtained dissolution times and their percentage values of the obtained dissolution time from measurement with room temperature DI H_2O as a solvent and the list of used parameters (solvent, temperature and stirring speed).

Optical measuring system												
Parameters	DI H_2O, rt, 350 rpm		Tap water, rt, 350 rpm		0.05M NaCl in DI H_2O, rt, 350 rpm		Cold DI H_2O, 350 rpm		Warm DI H_2O, 350 rpm		DI H_2O, rt, 250 rpm		DI H_2O, rt, 450 rpm	
Sample	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**
S1	24	100	18	73	70	292	36	150	-		32	133	20	83
S2	27	100	24	89	44	163	33	122	-		31	115	25	93
S3	41	100	42	103	102	249	44	107	-		42	102	30	73
S4	99	100	122	123	181	183	143	144	-		76	77	74	75
Torque stirrer														
Parameters	DI H_2O, rt, 300 rpm		Tap water, rt, 300 rpm		0.05M NaCl in DI H_2O, rt, 300 rpm		Cold DI H_2O, 300 rpm		Warm DI H_2O, 300 rpm		DI H_2O, rt, 200 rpm		DI H_2O, rt, 400 rpm	
Sample	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**
S1	12	100	13	104	22	183	10	83	8	67	9	75	8	67
S2	38	100	25	66	36	95	52	137	26	68	34	89	15	39
S3	15	100	26	179	48	331	19	131	11	76	17	117	17	117
S4	30	100	46	153	100	333	47	157	25	83	22	73	42	140
Rotational viscometer														
Parameters	DI H_2O, rt, 350 rpm		Tap water, rt, 350 rpm		0.05M NaCl in DI H_2O, rt, 350 rpm		Cold DI H_2O, 350 rpm		Warm DI H_2O, 350 rpm		DI H_2O, rt, 250 rpm		DI H_2O, rt, 450 rpm	
Sample	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**	**Time** (min)	**%**
S1	25	100	25	102	50	204	29	116	23	94	28	114	23	94
S2	22	100	23	105	38	173	26	118	23	105	26	118	25	114
S3	28	100	32	116	39	142	36	131	27	98	25	91	28	102
S4	66	100	78	117	99	150	76	115	47	71	36	55	122	185